



CFTRI-MYSORE



4190

Chemistry of woo.

1-1 in 100

100

81

T. C. M.

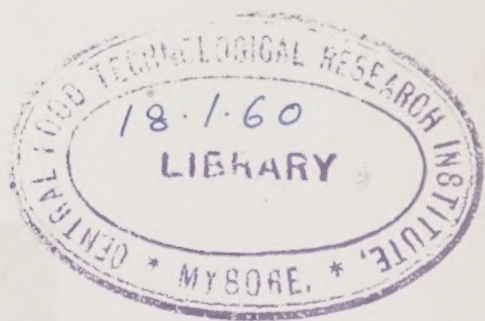


CHEMISTRY OF WOOD

Chemistry of **WOOD**

By **ERIK HÄGGLUND**

Swedish Forest Products Research Laboratory, Stockholm



1951

ACADEMIC PRESS INC., PUBLISHERS
NEW YORK, N. Y.

E1,58761J

N51

All Rights Reserved

No part of this book may be reproduced in any form, by photostat, microfilm, or any other means, without written permission from the publishers.

4190✓

CFTRI-MYSORE



4190

Chemistry of wood

PRINTED IN SWEDEN

ESSELTE AB

1951

000727

PREFACE

This book is a new, revised English edition of "Holzchemie," the first edition of which was published in 1928. Since the second German edition was published in 1939 great strides have been made in the various fields of wood chemistry. The results of this new research have greatly widened our knowledge and have necessitated a revision of many concepts held formerly. A comparison between this book and the previous edition clearly illustrates this fact.

Nevertheless, it was not considered necessary to change the general plan of the book to any great extent. As in earlier editions special attention has been paid to the chemistry of lignin and cellulose. Cellulose derivatives, however, fall outside the scope of general wood chemistry and since this subject has been excellently treated in several monographs it has been considered unnecessary to include the chemistry of derivatives in this work.

The expansion of this book in the new edition reflects the increased interest in problems pertaining to wood chemistry. Laboratory investigations in this field have been greatly stimulated by tremendous industrial developments which to a great extent depend on fundamental knowledge of the properties and behavior of the raw material under consideration. This reciprocity marks the way of progress especially in the pulp industry. The author has tried to keep this in mind in the preparation of this work. Thus, while emphasis is laid on the fundamentals of wood chemistry, the reactions involved in the processing of pulp have been discussed in the light of theoretical considerations. There is still much to be revealed by continued research. The utilization of waste products such as spent liquors constitutes one of the great problems still to be adequately solved. Increased knowledge with respect to the chemistry of lignin is the key to many industrial problems and especially for this reason much space has been given to this part of wood chemistry.

During the preparation of this book I have had the assistance of many persons, most of whom belong to the group of chemists with which I have had the pleasure of collaborating for many years. I wish, first of all, to express my indebtedness to Dr. E. Adler for his invaluable assistance in preparing the manuscript. He has critically read the entire text and has rewritten numerous portions, incorporating the results of the most recent research. Other co-workers were Civiling, H. W. Giertz, who prepared the chapter on bleaching, and Dr. L. Enebo, who wrote the section on the enzymatic degradation of cellulose. Dr. H. Erdtman wrote the section on "lignans" and made many valuable suggestions regarding the chapter on lignin. Dr. T. Enkvist has revised the chapter on alkaline pulping and Civiling, S. E. Häggglund the chapter on semi-

chemical pulping. Dr. P. W. Lange has written the section concerning the physical methods for the molecular weight determination of cellulose. I also wish to thank Dipl. ing. T. Johnson for his valuable advice regarding the technical processes, and Dr. H. Heiwinkel, Civiling. K. E. Ohlsson, and Dipl. ing. K. J. Björkqvist for their help with the Author and Subject Indexes.

I am indebted to Dr. Peter Oesper of the University of Pennsylvania for his excellent translation and to Dr. J. N. Ospenson for his assistance in revising the English of the various portions written since the initial translation. The excellent co-operation of the printer, Esselte AB, Stockholm, is gratefully acknowledged.

In conclusion, I wish to thank Academic Press for the far-sighted interest displayed in this work.

Stockholm,
April 1951.

E. Hägglund

CONTENTS

	PAGE
PREFACE.....	v
CHAPTER I. THE WOOD TISSUE.....	1
I. The General Structure of Wood.....	1
II. The Morphological Elements of Wood.....	4
III. The Arrangement and Volume of the Wood Elements.....	7
IV. The Growth of Wood.....	11
V. The Physiological Functions of the Wood Cells.....	17
VI. The Morphology of the Fibers.....	20
VII. Compression and Tension Wood.....	24
REFERENCES.....	27
CHAPTER II. THE PHYSICAL PROPERTIES OF WOOD.....	28
I. The Specific Gravity.....	28
II. The Water Content.....	31
A. Water Content of the Wood of Living Trees.....	31
B. Water Content of Air-Dried Wood.....	32
III. The Relation between Specific Gravity and Water Content.....	34
REFERENCES.....	36
CHAPTER III. THE WOOD COMPONENTS AND THEIR CHEMICAL PROPERTIES.....	37
I. The Components of the Woody Substance.....	37
A. History.....	37
II. Cellulose.....	41
A. The Structure of Cellulose.....	41
B. Changes Occurring in Cellulose by Swelling, Chemical and Enzymatic Attack, Heat, and Mechanical Treatment.....	77
1. Hydrate Cellulose.....	77
2. Hydrocellulose.....	78
3. Oxycellulose.....	81
4. Degradation of Cellulose by Mineral Acids.....	86
5. Cellulose and Alkalies.....	102
6. The Degradation of Cellulose by Heating in the Presence of Water..	103
7. The Degradation of Cellulose by Dry Distillation.....	106
8. The Enzymatic Degradation of Cellulose.....	109
9. The Strength of Fibers; Degradation by Mechanical Means.....	116
C. Cotton Cellulose and Wood Cellulose.....	118
D. The Determination of Cellulose in Wood.....	124
III. Wood Polyoses and Polyuronic Acids.....	134
A. Nomenclature.....	134
B. The Individual Wood Polyoses, Their Properties and Their Occurrence in Different Woods.....	137
1. Pentosan.....	137
2. Araban.....	142
3. Mannan.....	144
4. Glucan.....	148
5. Galactan.....	151
6. Fructan.....	153
7. Pectin.....	153
8. The Occurrence of Polyoses in Different Woods, their Dissolution and Determination.....	156
REFERENCES TO SECTIONS I, II, AND III (pp. 37—161).....	162
IV. Lignin.....	181
A. Introduction. Color Reactions of Wood.....	181
B. Properties of Native Lignin.....	193
1. Lignin, Extractable with Organic Solvents.....	193
2. Firmly-Bound Native Lignin.....	196

	PAGE
3. Reactions of Native Lignin with Sulfite.....	196
4. Reactions of Native Lignin with Hydrogen Sulfide and with Alkali Sulfides.....	212
5. Reactions of Native Lignin with Alcohols, Mercaptans, and Phenols.....	213
6. Reactions of Native Lignin with Halogens.....	214
7. Reactions of Native Lignin with Hydrogen Halides.....	214
8. Oxidation of Native Lignin.....	214
C. Lignin Preparations.....	215
1. Lignosulfonic Acid.....	215
a. Dissolution of Lignosulfonic Acid.....	215
b. The Properties of Dissolved Lignosulfonic Acid.....	218
2. Lignin Preparations Obtained by the Action of Alcohols, Phenols, and Various Organic Acids, Amines, and Hydrazine on Wood or Isolated Lignin.....	237
a. Alcoholysis of Wood. Alcohol Lignins.....	237
b. Phenol Lignins.....	246
c. Acetic Acid and Formic Acid Lignins.....	247
d. Thioglycolic Acid Lignin.....	252
e. Amines and Hydrazine.....	254
3. Alkali Lignin.....	255
4. Lignins Prepared by Extraction of Wood with Hydrotropic Solutions.....	261
5. Hydrol Lignin.....	262
6. Lignins Obtained by the Action of Mineral Acids.....	263
a. Sulfuric Acid.....	263
b. Hydrochloric Acid.....	264
7. Cuproxam Lignin.....	276
8. Periodate Lignin.....	278
D. The Degradation of Lignin.....	279
1. By Alkali.....	279
2. By Oxidation.....	280
3. By Hydrogenation.....	281
4. By Destructive Distillation.....	282
E. Summary of the Chemical Properties of Lignin.....	282
1. Elementary Composition and Functional Groups.....	282
2. Formation of Formaldehyde—The Absence of Methyleneedioxy Groups.....	290
F. Physical Properties.....	292
1. Light Absorption.....	292
2. Index of Refraction.....	294
3. Molecular Weight.....	295
G. Occurrence and Distribution of Lignin in Wood.....	297
H. The Constitution of Lignin, Biosynthesis of Lignin, Lignification.....	306
I. The Determination of Lignin.....	324
1. Isolation with Strong Acids.....	324
a. Sulfuric Acid.....	324
b. Hydrochloric Acid.....	327
c. Hydrogen Fluoride.....	328
d. Mixtures of Strong Acids.....	328
e. Hot, Dilute Mineral Acids.....	329
2. Indirect Methods for Determining Lignin.....	329
V. Minor Components of Wood.....	332
A. Resin, Terpenes, and Fat.....	332
B. Phenols, Tannins, Coloring Matter and Nitrogen-Containing Substances.....	343
C. Inorganic Components.....	347
D. Other Wood Components.....	349
VI. Analyses of Wood.....	350
VII. Physical Structure and Chemical Composition of the Fiber Wall.....	358
REFERENCES TO SECTIONS IV, V, VI, AND VII (pp. 181-366).....	367
CHAPTER IV. THE DECOMPOSITION OF WOOD BY ACIDS. WOOD SACCHARIFICATION	390

	PAGE
I. Introduction.....	390
II. Saccharification with Hot Dilute Acids.....	391
III. Saccharification with Concentrated Mineral Acids.....	400
A. Sulfuric Acid.....	400
B. Hydrochloric Acid.....	402
C. Other Procedures with Concentrated Acids.....	410
REFERENCES.....	411
CHAPTER V. THE PULPING OF WOOD WITH SOLUTIONS OF SULFUROUS ACID AND SULFITES.....	414
I. History of the Sulfite Process.....	414
II. The Theory of the Sulfite Pulping Process and its Practical Consequences.....	415
A. The Chemistry of Sulfite Pulping.....	415
1. Sulfonation and Delignification.....	415
2. Stability of Cooking Acid.....	424
3. Sulfate Formation.....	426
4. Loosely Bound Sulfur Dioxide.....	429
5. Formation and Destruction of Sugar During the Sulfite Cook.....	430
6. Available Sulfite and Color Change in Cooking Liquor.....	434
B. Sulfite Pulping with Other Agents than Calcium Bisulfite.....	436
1. Pulping with Sulfur Dioxide.....	436
2. Magnesium, Sodium and Ammonium Salts.....	437
C. Behavior of Different Woods.....	438
1. Wood Character and Pulping.....	438
2. Sulfite Pulping of Pine and Other Woods.....	443
3. Sulfite Pulping of Hardwoods.....	448
D. Properties of Sulfite Pulp.....	449
1. Pulping Conditions and Pulp Properties.....	449
2. Reddening of Pulp.....	451
3. Fluorescence of Pulp.....	455
III. By-Products of Sulfite Pulp Manufacture.....	456
A. Volatile By-Products.....	456
B. Utilization of Waste Liquor.....	458
REFERENCES.....	467
CHAPTER VI. THE PULPING OF WOOD BY AQUEOUS ALKALIES.....	474
I. History of the Alkaline Pulping Process.....	474
II. The Chemistry of the Alkaline Pulping Processes.....	475
A. Main Components of the Black Liquor.....	475
B. Alkali Consumption and Reaction Velocity in Cooks with Caustic Soda.....	476
C. The Effect of the Sulfidity in Sulfate Cooks.....	477
1. Rate of Delignification and Pulp Strength.....	477
2. Formation of Thioglignin.....	482
D. Demethylation of Lignin and Formation of Low-Molecular Fission Products.....	487
E. Alkali Cooks with Addition of Other Sulfur Containing Reagents than Sodium Hydrosulfide.....	488
F. Effect of Prehydrolysis of Wood in Alkaline Pulping.....	489
G. Sulfate Cooks of Hardwoods.....	490
III. The By-Products of the Alkaline Pulping Processes.....	490
REFERENCES.....	494
CHAPTER VII. OTHER METHODS OF PULPING.....	498
I. Semichemical Pulping.....	498
II. Pulping with Chlorine and Alkali.....	502
III. Pulping with Nitric Acid.....	503
REFERENCES.....	504
CHAPTER VIII. DELIGNIFICATION WITH BLEACHING AGENTS.....	506
I. Chlorination.....	508
II. Alkali Washing.....	516

	PAGE
III. Hypochlorite Bleaching.....	518
IV. Bleaching with Chlorine Dioxide and Chlorites.....	521
V. Bleaching and Pulp Characteristics.....	524
REFERENCES.....	528
CHAPTER IX. THE CHEMICAL PROCESS IN THE CARBONIZATION OF WOOD.....	531
REFERENCES.....	539
CHAPTER X. UTILIZATION OF WOOD BY CAUSTIC FUSION, PRESSURE HEATING WITH ALKALI AND DIGESTION WITH TARS OR PHENOLS.....	540
I. Caustic Fusion.....	540
II. Alkaline Pressure Heating.....	543
III. Digestion with Tars and Phenols.....	546
REFERENCES.....	547
CHAPTER XI. THE BEHAVIOR OF WOOD DURING STORAGE.....	548
REFERENCES.....	552
CHAPTER XII. THE NATURAL DECOMPOSITION OF WOOD.....	553
REFERENCES.....	562
AUTHOR INDEX.....	565
SUBJECT INDEX.....	616

CHAPTER I

THE WOOD TISSUE

I. The General Structure of Wood

By "wood" is meant the main tissue of the stems, roots, and branches of so-called "woody" plants, after the bark has been removed. Among these plants are included conifers, dicotyledonous trees and shrubs, and to a lesser extent, tree-like monocotyledons like the palms. The wood of the latter differs markedly from that of the other woody plants.

We are particularly interested in the wood of the conifers and deciduous trees. Examination of a cross-sectional cut of the trunk of any of these trees immediately reveals the following features:

The pith runs through the center of the stem and is more or less pronounced, depending on the type of wood. By far the largest part of the cross section consists of the wood proper, which is bordered on the outside by a thin layer of living cells, called the cambium. The cambium is surrounded by the inner bark or bast, and this, in turn, by the bark.

Even to the naked eye it is quite apparent that wood consists of various elements. Comparison of different types of woods sometimes reveals appreciable differences, but the main structural features are seen to be the same.

Most noticeable are the ring-shaped zones, which lie concentrically around the pith as center. These rings consist of alternate layers of more and less dense tissue. Each zone, consisting of both denser and lighter portions, corresponds to one year's growth in the woods of the temperate zones; the ring-shaped zones are therefore known as annual rings. The less dense part of the ring is the wood deposited during the spring, and is known as "early wood" or "springwood." This layer merges more or less sharply into the "late wood" or "summerwood," which is appreciably denser and darker in color. Formation of the summerwood stops late in the summer, and the formation of springwood commences again the next spring. The boundary between summerwood and springwood is generally quite definite, making the annual rings easier to distinguish. The annual rings are not, of course, equally distinct in all kinds of wood; while the conifers show clearly-marked annual rings, the deciduous woods (hardwoods) have much less sharply defined rings because

there is less difference in color between the springwood and the summerwood. A transverse section of hardwood shows quite distinct pores or holes. (For this reason, hardwoods are sometimes known as porous woods, while softwoods, or conifers, are termed nonporous.) These pores are crosscuts of so-called "vessels," which are tubular channels extending longitudinally through the trunk. In the so-called "ring porous" woods the vessels are much more prominent in the springwood, while "diffuse porous" woods have the vessels evenly distributed throughout the annual rings.

Occasional pores are encountered in certain softwoods; these are resin channels which have been cut across.

Besides the annual rings and the pores, the so-called medullary rays, which extend horizontally and radially, appear more or less clearly on a transverse section. Some of them, extending through all the annual rings, are known as "primary rays," while others, which arise in the later rings and run out to the outermost ring, are known as "secondary rays." The deeper a ray penetrates into the stem, the older it is.

Medullary rays are present in all types of wood, but are not always equally prominent. In some cases, especially in conifers, they are not visible to the naked eye.

In order to become fully acquainted with the structure of wood, it is necessary to examine radial and tangential longitudinal sections, as well as the transverse section (see Fig. 1).

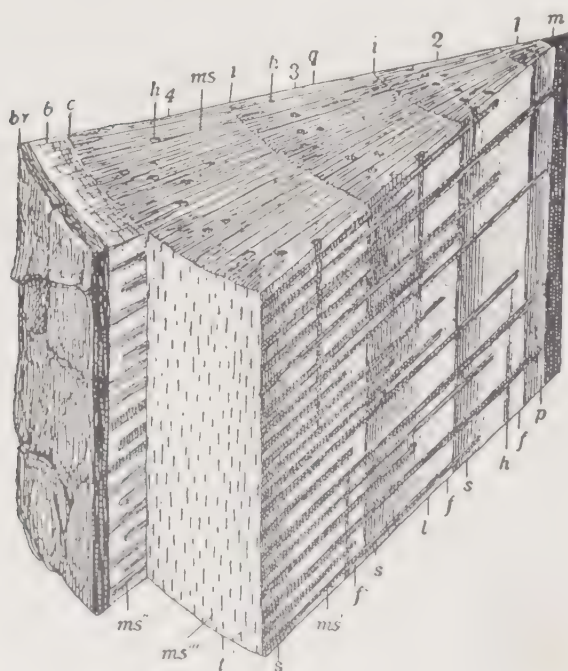


Fig. 1. Section of a four-year-old trunk of *Pinus silvestris*, showing a transverse section (top), a radial longitudinal section (right), and, where the bark has been removed, the tangential longitudinal section (front). Magnified about 6 times. (After Strasburger, Kultur der Gegenwart)

i, boundaries of annual rings; 1, 2, 3, 4, the four successive annual rings; *m*, the pith; *f*, the springwood; *s*, the summerwood; *c*, the cambium; *b*, the inner bark of the bast zone; *br*, the outer bark; *h*, resin canals; *ms*, transverse aspect of medullary ray; *ms'* radial section of medullary ray, appearing as a band; *ms''*, the same, seen in the inner bark; *ms'''*, tangential section of medullary ray.

The most obvious feature revealed by an examination of a radial section are the fibers which generally run longitudinally along the stem; this constitutes the most characteristic feature of the structure of the wood. The annual rings appear in radial section as parallel bands. Most hardwoods show fine furrows on the radial section, giving the wood a scratched appearance. These furrows are vessels that were cut open when the section was made, and may be straight or twisted in form. Coniferous woods have no vessels, and the surface does not appear to be scratched; only occasionally does a severed resin channel appear (Figs. 2 and 3.)

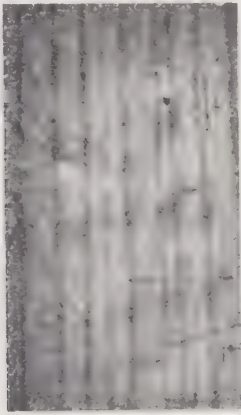


Fig. 2. Radial longitudinal section of pine wood. (After Dengler)

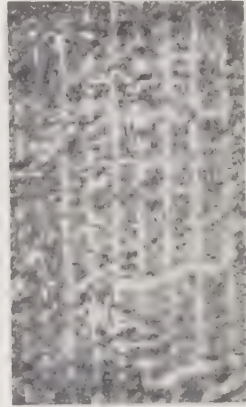


Fig. 3. Radial longitudinal section of beech wood. (After Dengler)

The medullary rays are also to be seen in the radial section, appearing here as bands, so narrow as to be invisible to the naked eye in coniferous wood, but quite broad and easily visible in many dicotyledons. The vertical extension of the rays is seen still more clearly in the tangential section (Fig. 4) where the cross section of the ray appears as a spindle-shaped (fusiform) structure. The rays do not run in exactly straight lines; hence a plane radial section gives only a part of the ray, which appears as a longer or shorter band (Fig. 3).

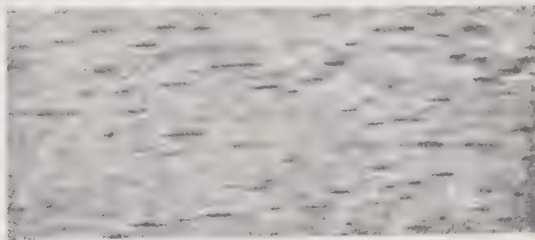


Fig. 4. Tangential longitudinal section of beech wood. (After Dengler)

shaped (fusiform) structure. The rays do not run in exactly straight lines; hence a plane radial section gives only a part of the ray, which appears as a longer or shorter band (Fig. 3).

II. The Morphological Elements of Wood

Wood is composed of cells or fibers which can be isolated by chemical means, for example, by a mixture of potassium chlorate and nitric acid. The cells are classified as prosenchymatous, and parenchymatous cells.

The prosenchyma is designed both for water transport and for giving mechanical strength to the wood. It involves vessels, tracheids, and libriform fibers.

The vessels arise by the longitudinal coalescence of tracheids which lie end to end in the stem; after the walls between the cells have been de-

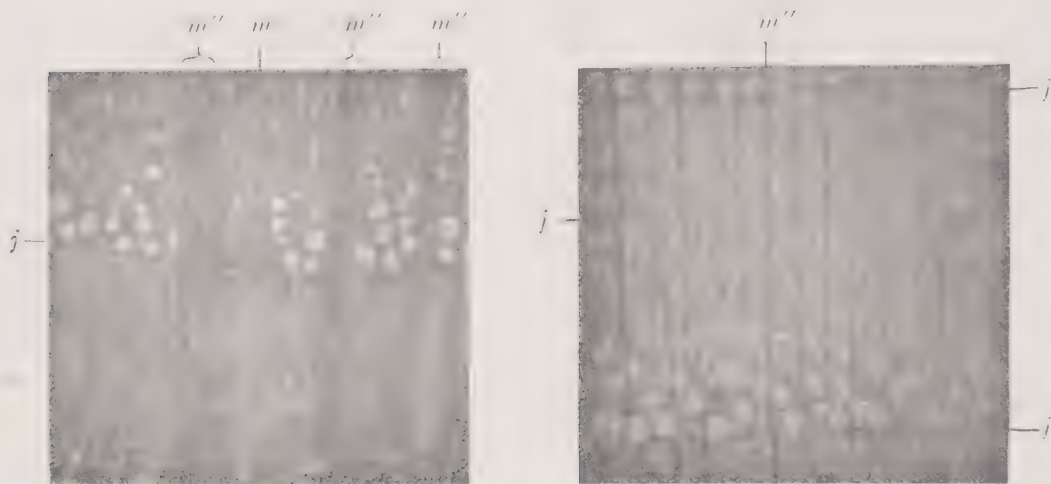


Fig. 5. Transverse section of oak. Transverse section of elm.
j, annual rings; *m*, uniseriate medullary rays; *m''*, multiseriate medullary rays.

stroyed, long tubes remain running through the trunk. The diameter of the vessels is quite variable even in a single specimen of wood (0.02-0.5 mm.) but it is generally true that the diameter is greater in springwood than in summerwood; see Fig. 5, taken from Dengler (1). The vessels usually have comparatively thick walls, and when they do not, the walls are covered with thickened ridges, in the form of spirals or of networks.

Vessels occur only in hardwoods, where they constitute the chief tracheal elements. Figure 6 (after Dengler) shows various types of vessels in linden (A), red beech (B and C) and oak (D).

The tracheids and the vessels have many points of similarity. The tracheids, however, in contrast to the vessels, consist of completely closed cells with pointed or rounded ends (Fig. 7, after Dengler). Vessel-like and fibrous tracheids may be distinguished.

Pits, which are characteristic both of vessels and of tracheids (Fig. 7 C), are thin places in the cell walls, round or elliptical in shape, surrounded

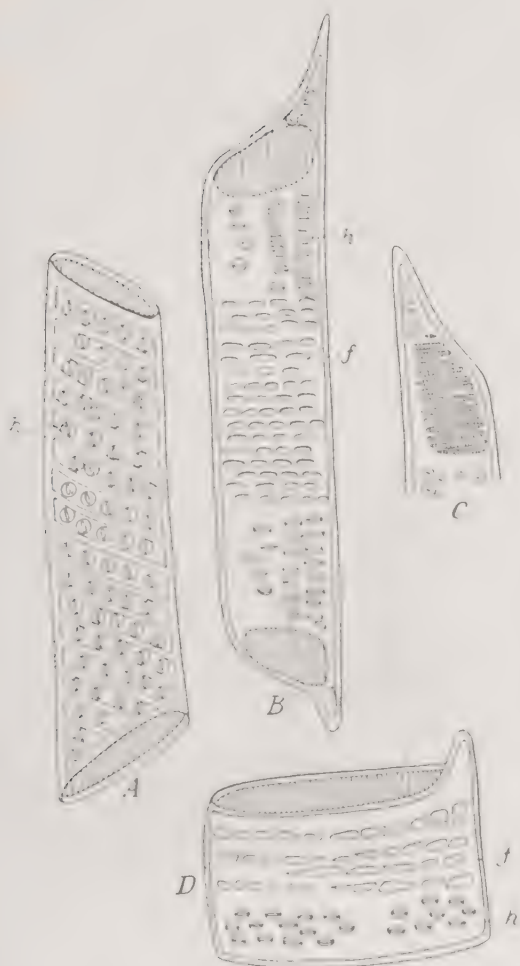


Fig. 6. Tracheal vessels, magnified 400 times. *A*, linden; *B*, *C*, beech; *D*, oak; *h*, bordered pits, showing the surfaces of contact between two pits; *f*, ordinary pits, showing the surfaces of contact with medullary rays.

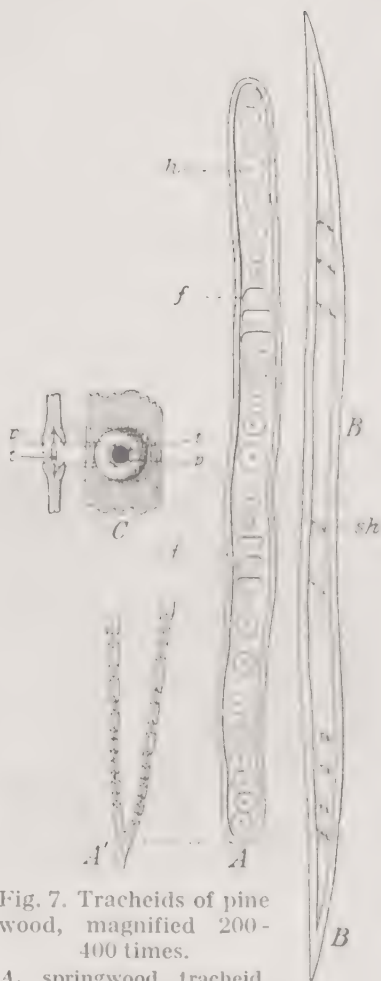


Fig. 7. Tracheids of pine wood, magnified 200-400 times.

A, springwood tracheid, shown in radial section. *A'*, same, tangential section; *B*, summerwood tracheid. *h*, bordered pit; *f*, ordinary pit; *sh*, slit-like bordered pit. *C*, side (left) and front (right) views of bordered pit. *p*, dome-shaped chamber; *t*, torus.

by thickened parts of the wall. They are usually "bordered," which means that the thickened parts of the wall surrounding the thin spot narrow down toward the inside of the cell, forming a dome-shaped antechamber (Fig. 7). The bordered pits are exactly matched by pits in adjoining tracheid cells. The thin-walled area thus formed between a pair of cells is thickened in the center; this thickened part of the membrane is called a "torus" and is so constructed that when pressure is put on one side of the membrane the torus fits up against the dome of the antechamber on the other side, and closes the opening. This arrangement probably serves as a valve, or pressure regulator.

The thin part of the wall has fine capillary openings which make possible the passage of water and aqueous solutions (2). Changes occurring during heartwood formation will be discussed later.

The tracheids have many pits, making the exchange of various materials possible. In conifers, which have no vessels, the transport of substances actually occurs exclusively through the pits, which are larger in this case. It should be emphasized, however, that in extensively lignified, thick-wall tracheids, for example, those occurring in the summerwood of conifers, the pits are smaller and much fewer in number. The appearance of the pits is also changed, becoming slit-like.

The libriform fibers occur only in hardwoods, but there they constitute the major portion of the body of the wood. The fibers are long



Fig. 8. Libriform fibers (after Dengler), magnified 200 times.

A, slightly thickened linden fiber;
B, much thickened beech fiber;
st, slit-like bordered pits.

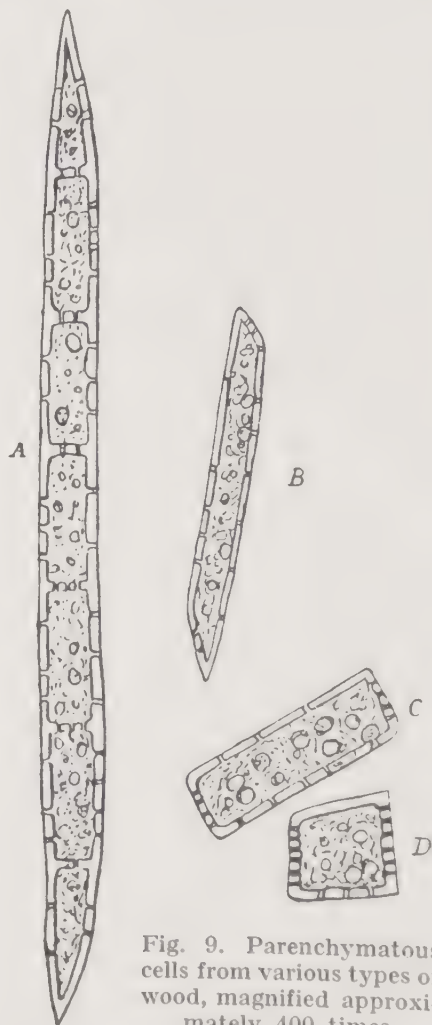


Fig. 9. Parenchymatous cells from various types of wood, magnified approximately 400 times.

A, ash, strand parenchyma; B, C, D, are ray parenchyma cells, B from beech, C and D from oak.

and narrow, with pointed ends and thick walls (Fig. 8, after Dengler) so that a longitudinal section of the cell appears as a thin slit. The length varies between 0.5 and 1.5 mm. The chief function of these fibers is to give mechanical strength to the wood.

The only living wood cells are the parenchyma. While the other cells contain mostly water and air, the parenchymatous cells contain living protoplasm, cell nuclei, metabolites, and reserve food, the latter consisting mostly of starch and fats. Deciduous trees store up most of the starch during the summer. In the case of spruce, it has been found that most of the starch disappears from the parenchyma during the spring when the buds open, and is replaced by fat. In the fall the starch is again stored up (3).

The parenchymatous cells sometimes contain dyestuffs, too, and resin is present in coniferous woods. The parenchyma of heartwood is largely dead.

As far as the appearance of the parenchyma is concerned, it consists either of short, prismatic cells which appear rectangular in longitudinal section, and which may be replaced by longer cells, pointed at the ends, or of longitudinal parenchyma strands which are sometimes divided into compartments by cross walls.

The short parenchymatous cells are usually arranged in longitudinal series to form parenchyma strands of fibrous appearance (see Fig. 9). A is strand parenchyma from ash, B-D are ray parenchyma cells, B from red beech, C and D from oak.

III. The Arrangement and Volume of the Wood Elements

The various types of cells form connected systems which run through the whole body of the wood. There is also a certain connection between the vessels and the parenchyma cells. The various types of tissues occur in very different relative amounts in various parts of the stem. The form of the cells is not always the same, either.

The percentages of the volume occupied by the various tissues in different woods are important in the technical utilization of wood, both from the standpoint of the strength of the wood, and from that of the value of the wood for chemical pulping procedures.

Of the more recent investigations, those of B. Huber and G. Prütz (4) may be quoted. They have calculated the volume percent of various tissues in different woods, making use of an integrator. The following figures may be given from their results:

	Volume percent			
	Fibers	Wood Rays	Wood Parenchyma	Vessels
Spruce (<i>Picea excelsa</i>)	95.3 (94.5-96.5)	4.7 (4.4-5.3)		
Pine (<i>Pinus silvestris</i>)	93.1 (93.3-95.6)	5.5 (4.4-6.7)	1.4 (0.0-5.8) ¹	
Larch (<i>Larix europaea</i>)	91.2 (89.0-93.0)	8.8 (7.0-11.0)		
Fir (<i>Abies peccinata</i>)	90.4 (88.0-91.6)	9.6 (8.4-12.0)		
Horse chestnut (<i>Aesculus hippocastanum</i>)	76.1 (74.2-78.0)	15.5 (13.1-16.8)		8.4
Birch (<i>Betula verrucosa</i>)	64.8 (59.6-68.1)	10.5 (9.7-11.1)		24.7
Ash (<i>Fraxinus excelsior</i>)	62.4 (50.5-72.4)	14.9 (13.9-16.0)	10.6 (5.7-15.1)	12.1
Aspen (<i>Populus tremula</i>)	60.9 (59.3-62.5)	12.7 (11.1-13.5)		26.4
Oak (<i>Quercus pedunculata</i>)	58.1 (53.5-63.3)	29.3 (25.1-33.0)	4.9 (2.8-6.1)	7.7
Beech (<i>Fagus silvatica</i>)	37.4 (34.5-43.6)	27.0 (22.6-30.0)	4.6 (4.0-5.5)	31.0

¹ Resin ducts.

It may be noted that variations occur within a single annual ring; these are of course caused primarily by the fact that more space is occupied by the vessels in the springwood than in the summerwood.

The pith consists of parenchymatous cells of different shapes. It is softer than the wood, and is usually circular in cross section although its shape varies; it is often polygonal.

In radial sections the wood rays appear as radial bands composed of one or more rows of cells. The individual cells have a rectangular outline, usually elongated, hence they can be considered as running in the direction of the rays. The positions of the ray cells with reference to each other is like the arrangement of the stones in a wall. These cells are parenchymatous. In certain conifers such as spruce, pine, larch, hemlock, etc., the rays also contain tracheids. The ray tracheids in these woods transport foodstuffs in from the bast, and water out from the center of the stem. The rays are accompanied by hollow intercellular spaces filled with air, the so-called "intercellular passages" that are narrow in uniseriate (single-layered) rays, but wider in multiseriate rays, where they frequently constitute resin ducts, at least in conifers (Fig. 10).

The elements of the wood and their arrangement can be quite different in different kinds of wood. The simplest and most regular arrangement is found in coniferous wood, which contains only tracheids, wood rays, and strand parenchyma. The tracheids are ordered in radial rows, each of which is derived from a single cambium cell. In deciduous wood this

regularity is not found because the broad vessels have disturbed the arrangement of the cells.

Observation of a transverse section of softwood reveals that the tracheids which are arranged in radial rows appear to have four to six sides (see Fig. 18). The wood rays run between these rows, their cells appearing here in longitudinal section. The tracheids of the springwood are broad and thin-walled, and have large, bordered pits only on their radial side walls (Figs. 10, 11). The smaller tracheids of the summerwood are flattened, have thicker walls and bordered pits on the tangential walls as well as the radial walls. The tracheids of the summerwood and those of the next year's springwood are thus sharply differentiated. The rings, of course, run perpendicular to the radial rows of cells. In a tangential section the tracheids are cut at various heights, the pits are shown in cross section, and the tracheids exhibit pointed ends, while a radial cut reveals the pits in side view, with the tracheids showing rounded ends. The tracheids of hardwoods differ from those of conifers in that they are pitted on all sides.

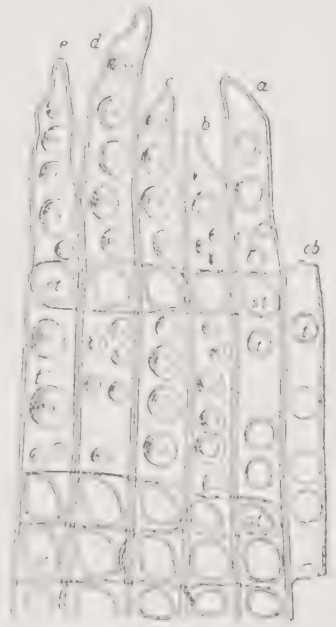


Fig. 10. Part of a radial longitudinal section of the trunk of *Pinus silvestris*, magnified approximately 400 times. Taken from Frank's textbook (After Sachs).

cb, cambial wood cell; *a—e*, old wood cells; *t*, new bordered pit; *t'*, old bordered pit; *st*, large pit at the boundary between a medullary ray cell and a wood cell.

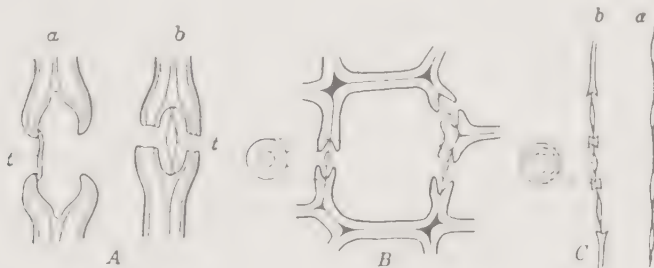


Fig. 11. Structure and development of a bordered pit in pine wood.

A, cross section through the pit, *a*, in springwood, *b*, in summerwood. *B*, cross section through a tracheid having bordered pits in the radial walls; a front view of a pit is shown at the left. *C* (*a* and *b*), successive stages in the development of the pits, seen in tangential longitudinal section.

The woods whose rays contain resin canals always have similar resin ducts running through the wood longitudinally; the ducts intersect the rays perpendicularly and form a connected system with them.

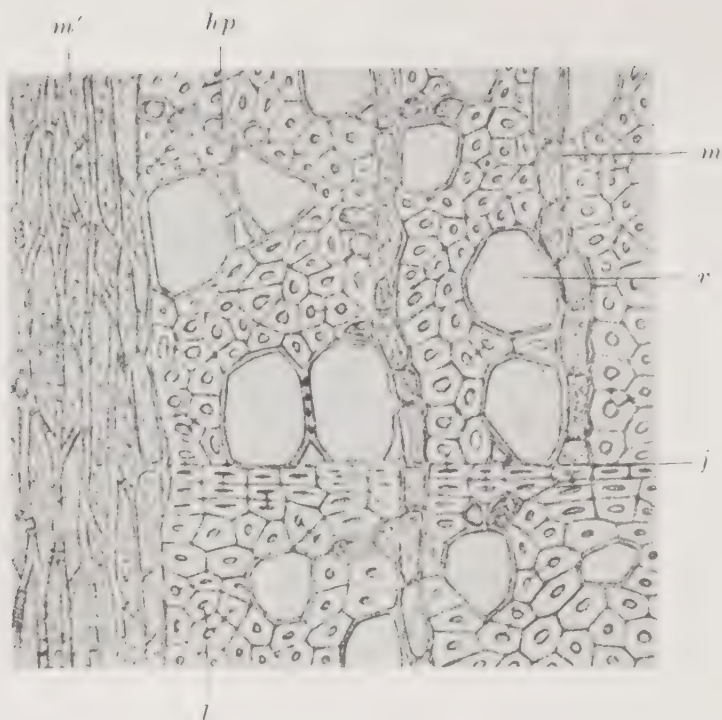


Fig. 12. Transverse section of red beech wood, magnified 400 times.
v, vessels; *l*, libriform fibers with slit-like pits; *hp* wood parenchyma, *m*, uniseriate medullary ray; *m'*, multiseriate medullary ray; *j*, boundary between annual rings.

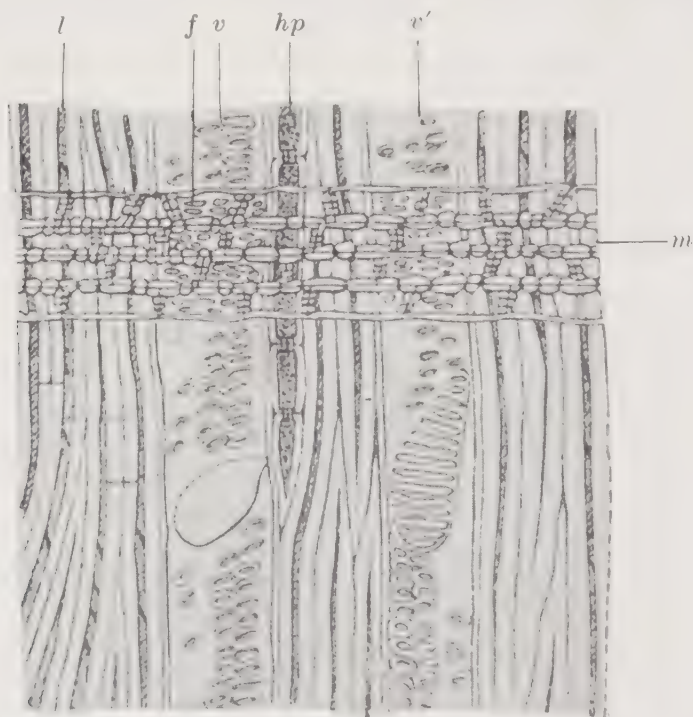


Fig. 13. Radial longitudinal section of red beech wood, magnified 400 times.
v, vessel with circular perforation; *v'*, vessel with latticed perforation; *l*, libriform fiber with slit-like pits; *hp*, wood parenchyma; *m*, wood ray, with simple pit at *j*. The medullary rays are represented as blank regions, in the interest of clarity.

Cross sections of hard and coniferous woods are quite different in appearance, as has already been mentioned. The radial arrangement of the cells is obscured in deciduous wood and most of the cells consist of libriform fibers.

Vessels are characteristic of hardwoods, and are easily seen by contrast with the narrow fibers (Figs. 12, 13). The vessels are sometimes distributed fairly evenly over the entire surface of the wood, and sometimes localized in certain spots. Springwood contains more vessels than summerwood, and their breadth is also greatest there, decreasing more or less suddenly in the summerwood. If the decrease is gradual, the wood is known as "diffuse porous," and if sudden, as "ring porous." Examples of diffuse porous woods are birch, alder, cherry, and red beech, whereas oak, ash, and elm are examples of ring porous woods. (Figs. 5, 14).

Longitudinal or wood parenchyma cells usually occur as strand parenchyma in hardwood, and occasionally appear in considerable quantities, as may be seen from the table on p. 8. They often border on the vessels, as is shown in Figs. 12 and 13.

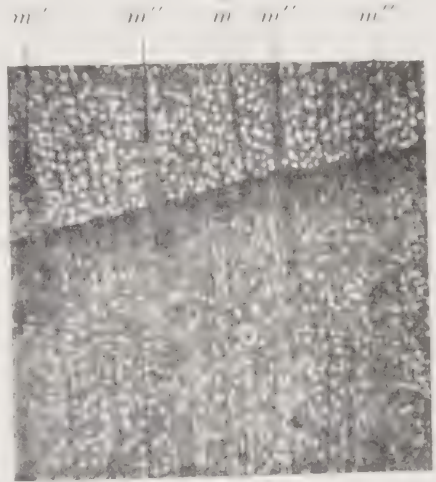


Fig. 14. Transverse section of red beech wood.

j, boundary between annual rings; *m*, uniseriate medullary ray; *m''*, multiseriate medullary rays.

IV. The Growth of Wood

A great deal of information concerning the growth of the woody tissue will be obtained by studying the young shoot of a woody plant. The



Fig. 15. Enlarged view of a bud of silver spruce. Left, the tip of the shoot seen from above, with the active growing center in the middle. Right, longitudinal section of same.

tip of the shoot, seen under the microscope, is usually round, and covered with bud scales. The bud is soft and succulent, and very active growth occurs here by cell division (Fig. 15). The various elements characteristic of the stem arise by this process.

On the outer part of the tip of the shoot cells are formed having a different appearance from the cube-shaped ones of the original tissue. In certain of the cells oblique walls form, from which longitudinal cells arise by "gliding growth" (cf. Fig. 17). Together, these form a closed ring (seen in cross section) called the "procambium." The cambium cells increase in number by division. From a cambium cell two identical cells at first arise, of which the one lying toward the center of the tree becomes lignified, forming "primary wood." The other cell, lying toward the outside of the tree, forms a cell of the "primary bark" or bast (phloem). One of the cells, however, always remains capable of dividing; all of these mother cells together form a thin growing-layer, one cell in thickness, called the "cambium." In the manner described above there arise the so-called primary wood and primary bark or phloem; continued division of the cambium cells gives rise to further wood and phloem cells, the secondary wood and bark.

As the cells are formed inside the cambium, the cambium itself moves outward. In order for the cambium to continue to form a closed ring, it is necessary for the number of cambium cells to increase. This actually occurs. In this process, the cell division does not give rise to new wood or phloem, but to new cambium cells, which enter into the cambium ring. The diameter of the cells also increases. The activity of the cambium cells results in the formation of more wood cells than phloem cells. Since the phloem cells are also compressed by bark pressure, while the wood cells retain their original size, it is easily seen why the bark makes up only a small fraction of the total volume of the stem in older trees.

Besides the wood and phloem cells, there is also formed at certain places in the cambium a quite different type of cell, namely wood ray (medullary ray) cells. These are elongated parenchymatous cells, lying perpendicular to the direction of the stem, and thus giving rise to radial bands running from the bark into the tree. Cambium cells lying above one another frequently form ray cells at the same time, and cambial cells lying next to one another sometimes do so; the multi-layered (multi-seriate) wood rays are formed thus. For this reason the rays usually appear as narrow vertical bands.

The division of the cambium cells results in growth of the stem in thickness, with phloem cells being formed outside the cambium, and wood cells, inside the cambium (Fig. 16). Since these processes continue

as long as the tree lives, the thickness of the trunk and of the branches increases continuously.



Fig. 16. Portion of a cross section of a pine trunk, showing the border between wood and bast. (After Strasburger)



Fig. 17. Simplified drawings of the cambial cells. Top (a-b), simple cells, seen from various angles. Bottom (c-d), cells with pointed ends, before and after the onset of "gliding growth."

A longitudinal section of the cambium reveals that the cells have an elongated form from the very beginning, and that they are pointed at the ends (Fig. 17).

When these cells are young they have the shape shown in Fig. 17 c, but as they grow they extend themselves greatly in the longitudinal direction, the ends of adjoining cells sliding past one another ("gliding growth"). Investigations have shown that special growth hormones, called auxins, are effective in causing this behavior (5).

The cambium forms, then, three types of cells. There are first of all the wood cells, which give strength to the trunk, secondly, the phloem or bark with its sieve tubes, which conduct the sap to the cambium, and finally, the ray cells, which serve both for conduction and for storage.

Remarkably enough, the cells often deviate considerably in appearance and dimensions from the cambium cells from which they were formed. This is most obvious in the case of the vessels of deciduous woods. In this

case the daughter cells have a diameter which is of a quite different order of magnitude from that of the mother cells; the vessels therefore force the other cells (wood and wood ray cells) out of their radial alignment (Figs. 5 and 12).

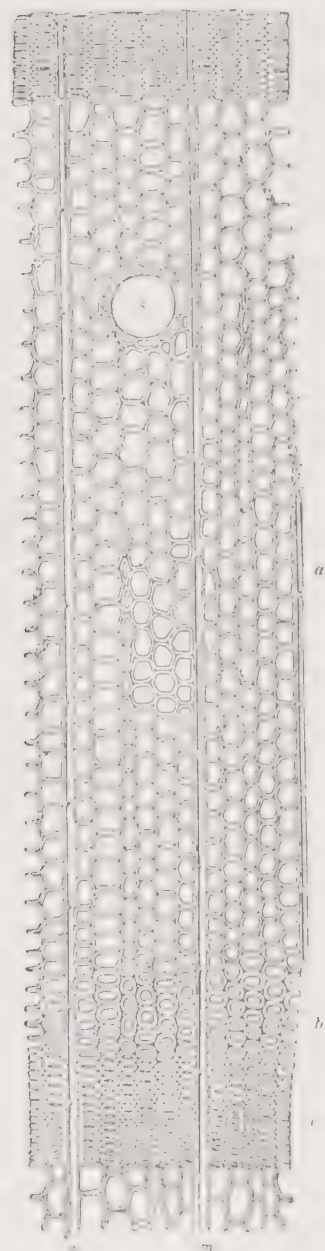


Fig. 18. Portion of a cross section of *Pinus* trunk. *a*, springwood; *bc*, summerwood; *s*, resin duct; *mm*, medullary rays.

Cells of varying dimensions, varying forms, and unequal lignin content are formed because of varying growing conditions at different times of the year. The broad, thin-walled cells of the springwood are usually quite easy to distinguish from those of summerwood, so that there appears, as has already been mentioned, a distinct boundary between the cells laid down in two successive growing seasons (boundaries between the annual rings) (cf. Fig. 18).

The annual rings are particularly clear in coniferous woods (Fig. 19). In the case of hardwoods they are not always so sharply outlined; the differences caused by the variations in the vessels are more definite, as has already been emphasized.

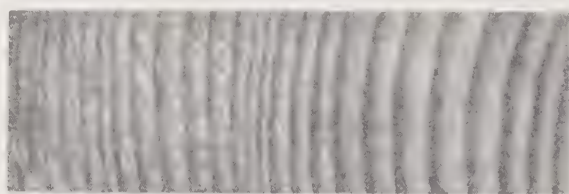


Fig. 19. Transverse section of larch wood, showing the annual rings. The dark layers are summerwood, the light layers, springwood.

The breadth of the annual rings is quite variable, depending on the kind of wood and on the growing conditions. It has been found that in the case of softwoods the percent of summerwood in the ring decreases with increasing breadth of the rings. The opposite is true of hardwoods.

The older, inner wood of many types of trees, both coniferous and deciduous, is denser, and has a higher content of solids and a lower content of water than the younger wood. This

is often reflected in a darker color. This inner wood is known as "heartwood," while the outer wood is called "sapwood." Other characteristics of the heartwood are its higher density when dry, its smaller capacity for taking up water, (which is important when the wood is floated down streams) and its higher resistance toward other external agencies. The formation of heartwood in some conifers is accompanied by an increase in the fat and resin contents of the tracheids.

In several cases, the extractives contained in heartwood have been shown to possess fungicidal properties, which explains the greater durability of such wood (cf. Chapter III, p. 343). Certain phenolic constituents, like pinosylvin and taxifolin, inhibit the sulfite pulping of the corresponding heartwoods (cf. Chapter V, p. 444).

The changes in the wood which are characteristic of heartwood formation begin only when the tree has reached a certain age, and proceed to the extent that the water-conducting systems are no longer required for life and growth. This depends primarily upon the age of the tree, but other factors are also involved. It should be remembered that the crown of the tree ceases to enlarge after a certain time, but that the formation of new annual rings continues nevertheless. The interior of the stem is not needed for water-conduction after this point has been reached. Secondary processes are also involved in the formation of heartwood; among these are the deposition of resins and other materials which stop up the pores and channels of the wood.

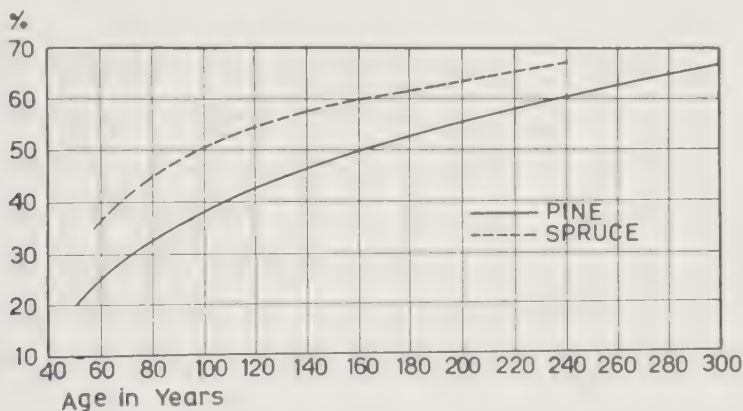


Fig. 20. Percentage of heartwood as a function of the age of the tree.

Figure 20 shows graphically the connection between the age of pine and spruce woods and the percentage of heartwood (6).

Investigations by E. Hågglund and his co-workers (7) have shown that the age at which heartwood formation begins in pine trunks is practically the same for all trees in the same geographical location,

but that the age rises at higher latitudes. In Southern Sweden the heart-wood formation begins at 25 years, for example, while in Central Sweden it begins at 40 years, and in Northern Sweden, only at 70 years.

Simultaneously with the growth in thickness, elongation of the shoot occurs, and a new bud is formed before the growing season ends. This bud can form a new shoot during the next season, thus lengthening the main stem, or it can die. In the latter case, the growth in length will be carried on by another bud which grows out from the side of the original stem. Continued growth of the original stem results in the straight trunk and branches characteristic of conifers; when the terminal buds die, more or less crooked branches result, as is often the case with hardwoods.

For the sake of completeness the following point should also be noted in connection with the formation of woody tissue. It has already been said that new wood cells are formed by cell division. This occurs by growth of

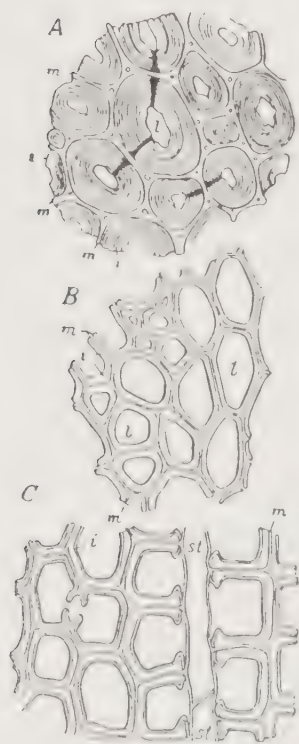
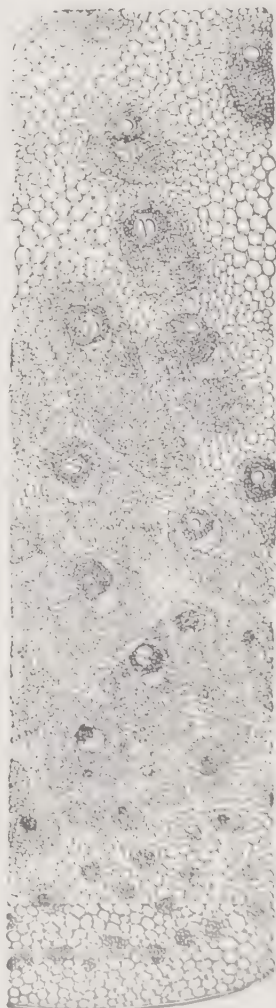


Fig. 21. Cross sections of cells.

A, bark of the stem of *Lycopodium chamaecyparissus*. B, wood cells from the inner part of the wood of a young woody fiber of *Helianthus annuus*. C, wood of *Pinus silvestris*, st, medullary ray; m, middle lamella; i, membrane lying next to the middle lamella; l, lumen of the cell, with the contents removed.

Fig. 22. Transverse section of a portion of a palm trunk, magnified 30 times. (After Drude)



a new wall or partition through the cell. Such a partition does not at first consist of two separate layers, but of a single thin membrane. A thickening of the wall occurs by deposition of material from both sides, giving each cell its own membrane. A cross section through the wall therefore reveals three layers, of which the middle layer has been termed the "middle lamella" by J. Sachs (8). (The three layers together are sometimes called a "compound middle lamella." See Fig. 21.)

As previously mentioned, the inner bark and cambial zone of a tree contain living cells, that are active in its life processes and growth. A chemical analysis of these zones in comparison with the other parts of the wood tissue has recently been carried out by E. Anderson and W. W. Pigman (9). It reveals typical differences between the living and the mature tissues, the former being characterized by a relatively high protein and low lignin content (cf. following table).

Analyses of Fractions of Black Spruce
(On the Oven-Dry Basis)

	Outer Bark	Inner Bark	Cambial Zone	Young Sap- wood	Sap- wood	Heart- wood
Ash, %.....	1.20	3.18	3.57	0.37	0.30	0.28
Nitrogen (Kjeldahl), %.....	0.32	0.60	1.09	0.26	0.05	0.06
"Protein," (N \times 6.4), %.....	2.05	3.84	7.06	1.66	0.32	0.38
Pentosans, %.....	11.80	12.03	6.30	8.12	12.05	12.45
Uronic anhydride (CO ₂ \times 4), %	8.56	10.00	4.60	3.80	3.72	3.92
Lignin (Klason method) in:						
Unextracted material, %.....	33.9	6.6	1.83	24.9	26.3	26.1
Extractive-free material, %..		9.00	6.03			
Methoxyl, %.....	4.00	2.19	0.72	4.73	4.89	4.75
Tannin (A.O.A.C. method) %	1.9	7.6	Neg.	Neg.	Neg.	Neg.
Starch test (iodine color).....	Neg.	Pos.	Neg.	Neg.	Neg.	Neg.

The structure of the woods of the conifers and deciduous trees discussed above differs widely and fundamentally from that of the tree-like monocotyledons, such as the palms. A crosscut of a palm trunk shows a large number of bundles of vessels enclosed among the libriform fibers. The bundles of vessels increase in number toward the outer part of the trunk, but are otherwise distributed quite at random. They do not change appreciably in the course of time. The increase in thickness of the palm trunk does not occur because of the activity of a cambium layer, but usually by increase in the size of the cells of the main tissue, or of the spaces between the cells (cf. Fig. 22).

V. The Physiological Functions of the Wood Cells

It has already been explained that the different cells in the woody tissue have different physiological functions. Thus one can distinguish:

1. The system for conducting water: vessels, tracheids, rays
2. The system for imparting mechanical strength: tracheids, libriform fibers [or hard fibers, as they have been called by R. Trendelenburg (10)]
3. The system for storage: wood parenchyma and wood rays.

The function of the water-conducting or tracheal system is to convey water and the materials dissolved in it from the roots to the crown of the tree. Botanists are not sure what forces are involved in this process, whether, for example, they be osmotic pressure, capillary action, evaporation, or others. There is, however, no doubt that most of the water passes up through the tracheids and vessels; the form and arrangement of these elements is exceptionally well suited for water-carrying. It has already been emphasized that there is considerable difference between the tracheal systems of the conifers and the hardwoods. The long, open, and broad vessels of the hardwoods make possible the very easy passage of water; this is indeed necessary, since the hardwoods, especially during leafing, require large quantities of water. The water requirements of the conifers are more uniform. In the conifers the conduction of water is appreciably more difficult, for the passage of the water from one tracheid to another through the membranes of the pits is not so easy as that through the open channels of the vessels of hardwoods. Libriform fibers and wood parenchyma are of less importance for water conduction.

The tracheids of conifers have a second purpose: the strengthening of the wood. The summerwood tracheids are particularly important here, and the greater the proportion of the wood which consists of such tracheids, the greater will be its mechanical strength.

The same thing may be said of the libriform fibers of the hardwoods, which correspond mechanically to the summerwood tracheids. The libriform fibers and the tracheids of summerwood are characterized by small interior cavities and thick walls. Hence woods which are rich in these fibers have a relatively high specific gravity, and the density of the wood is to a large extent an indication of its strength. A very strong, interlocking growth of these fibers is made possible not only by the great strength of these elements, but also by their shape, which is characterized by sharply pointed ends.

The third tissue of the wood consists of the wood and ray parenchyma. With the exception of the cells still in the process of development, these are the only cells in the wood which are alive. In all coniferous woods the tracheids constitute the great bulk of the wood; the parenchyma is quite negligible, and only the rays occupy as much as 10 % of the volume. In hardwoods the rays reach 30 %, and the wood parenchyma about 10 %.

of the volume (cf. p. 8). In some tropical woods as well as in the wood from roots, however, higher contents of parenchymatous cells have been observed (4).

The parenchyma has the function of storing and exchanging materials. The substances which come from the sap or from the leaves of the tree, or which are formed or consumed in the parenchyma consist, among other things, of certain carbohydrates, starch, wood gum, fats, oils, and resins.

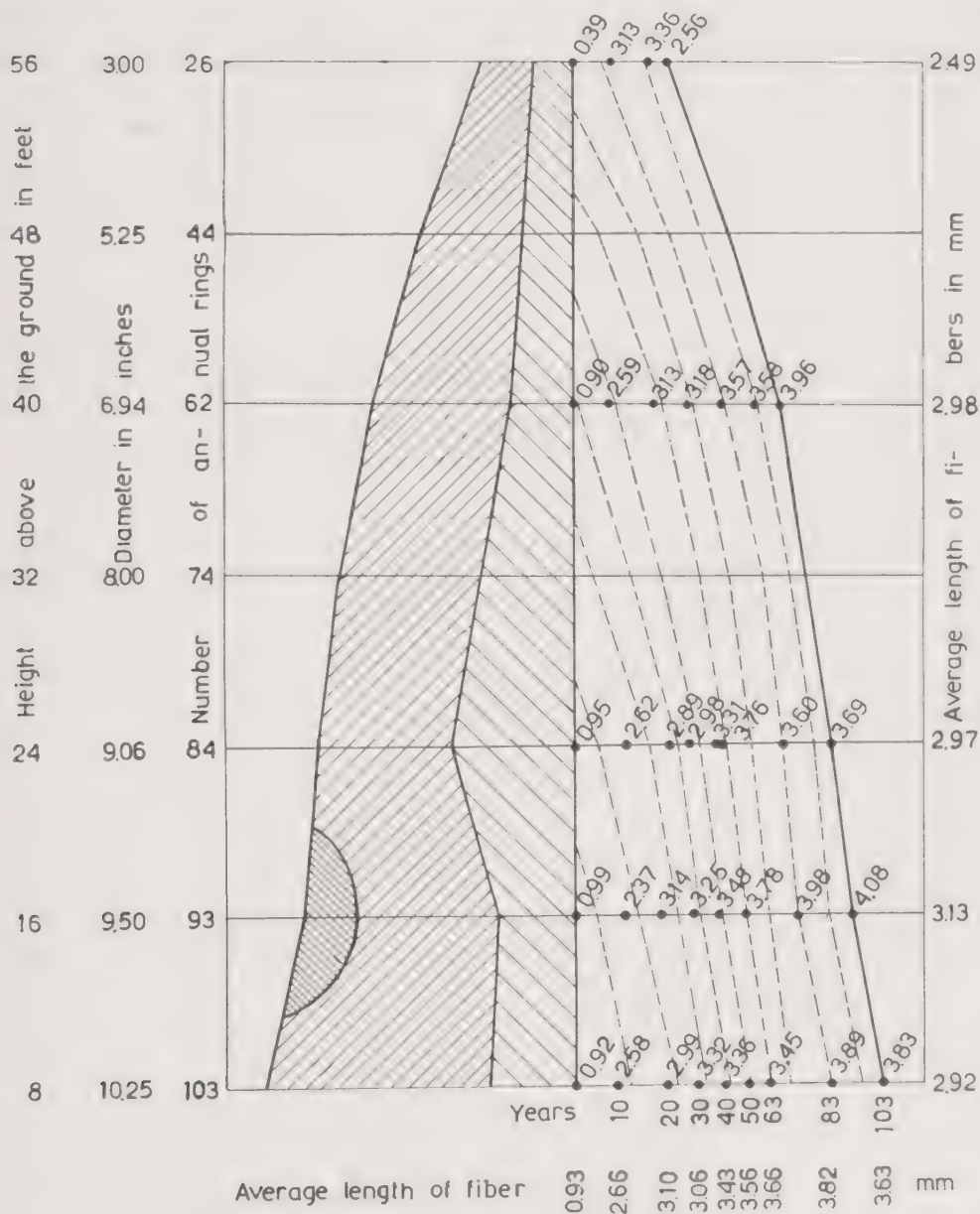


Fig. 23. Fiber lengths in various portions of the trunk of the black spruce (*Picea mariana*).

VI. The Morphology of the Fibers

The question of the length and breadth of the fibers is of both scientific and practical interest. As has already been said, the fibers are of quite different sizes. The variations are apparent not only when different types of wood are compared, but also within a single stem. The fibers of the conifers are in general significantly larger than those of hardwoods, averaging 3 mm. in length as compared with 1 mm. The ratio of length to breadth varies in different annual rings, and even from spring- to summerwood within the same ring.

The variation in fiber length is illustrated in Fig. 23, which refers to "black spruce" (*Picea mariana*) (11).

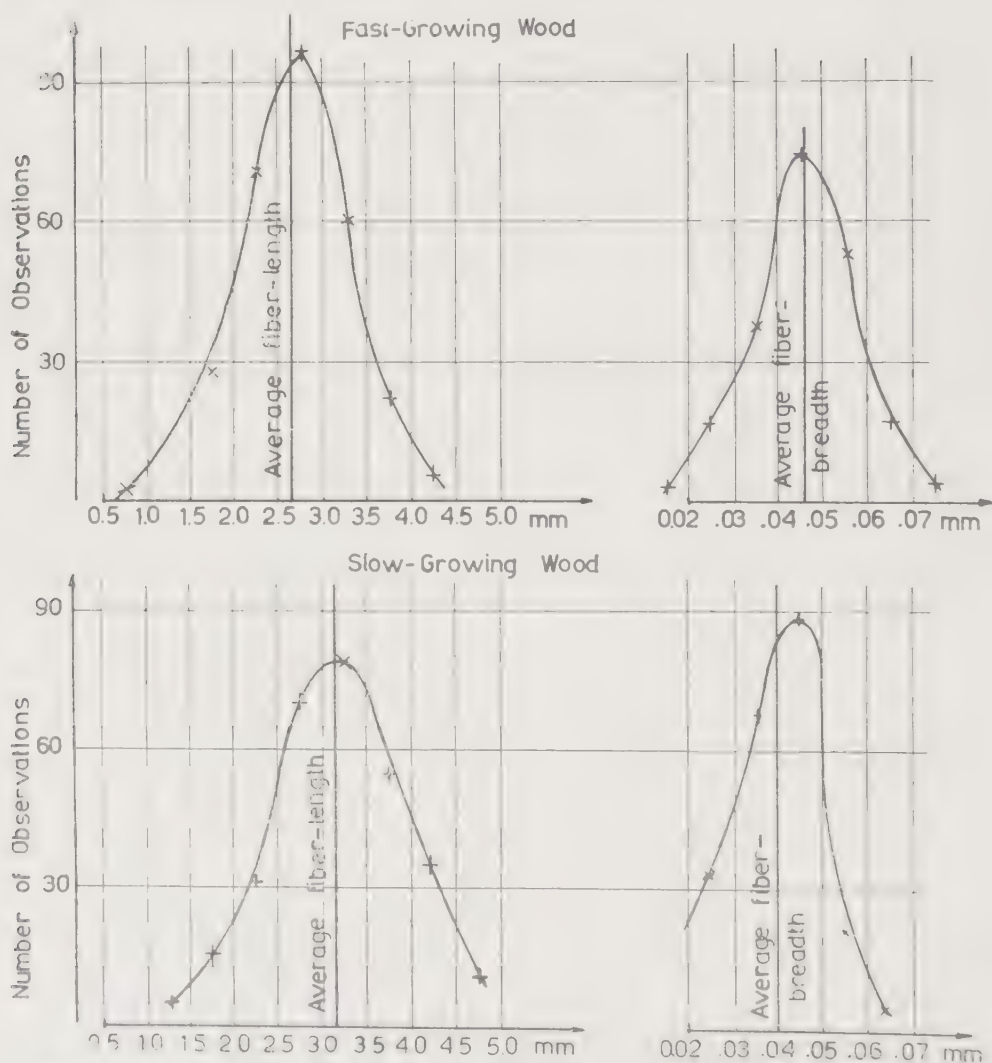


Fig. 24. Distribution curves showing the lengths and breadths of the fibers of spruce (*Picea excelsa*).

The diagram indicates that the average length of the fibers increases up to a certain height on the trunk, and then decreases again. This is also true of ordinary spruce and pine, though not to so marked an extent.

The average length and breadth of the fibers is important in technology. Measurements on spruce and pine were made by E. Hägglund and his co-workers (12). The wood was pulped with alkali under pressure and the pulp disintegrated to fibers. The length and breadth of the fibers were measured, and the fibers separated into groups with 0.5 mm. difference in length. Fibers between 5.5 and 6 mm. long were only rarely observed. The breadths were divided into groups separated by 0.01 mm. Graphical representation of the distribution makes it possible to determine how many measurements must be made in order to eliminate the random errors. From the number of fibers in each group and the average length in the group, the total length of all the fibers of the group is calculated. The sum of the lengths of all fibers, divided by the total number of fibers, gives the average fiber length. The average breadth is determined in the same way. Examples of the frequency curves for length and breadth of fibers from fast- and slow-growing spruce are given in Fig. 24. The fibers of the fast-growing wood are seen to be short and broad; the ratio of length to breadth is 45-60, while the ratio for slow-growing spruce may run as high as 90. This is also evident from the table below:

Sample (of Spruce)	Number of Annual Rings per cm.	Density of Wood (Dry)	Average Length (L) of Fibers mm.	Average Breadth (B) of Fibers mm.	Ratio L : B
Fast-growing....	1.7	0.28	2.22	0.050	44
"	1.4	—	2.49	0.050	50
"	2.5	0.32	3.04	0.048	63
"	2.0	0.31	2.64	0.046	57
Slow-growing....	18.5	0.40	3.78	0.041	92
"	17.4	0.42	3.45	0.040	86
"	23.2	0.40	3.35	0.039	86
"	17.3	0.40	3.19	0.040	80

Greater variations in the length of the fibers are observed with pine than with spruce, but the average breadth of the fibers proved to be relatively constant. The following figures may be quoted:

Sample (of Pine)	Number of Annual Rings per cm.	Density of Wood (Dry)	Average Length (L) of Fibers mm.	Average Breadth (B) of Fibers mm.	Ratio L : B
Fast-growing....	2.8	0.36	2.23	0.044	51
"	2.8	0.40	2.47	0.041	61
"	2.8	0.36	1.81	0.044	41
"	2.0	0.36	1.81	0.037	49
Slow-growing....	12.0	0.45	2.48	0.038	66
"	14.0	0.40	2.40	0.036	66
"	29.0	0.44	2.68	0.035	77
"	21.0	0.39	3.22	0.037	86
"	18.0	0.39	2.85	0.036	79

Here too, it may be seen that slow-growing wood contains longer and thinner fibers than fast-growing wood. A comparison of pine and spruce shows that the spruce fibers are appreciably longer than those of pine. Since the breadth of the fibers is nearly equal, the ratio of length to breadth is greater for spruce.

It may be said in general that the average length of the fibers depends on the place where the trees are grown, to the extent that wood grown in colder climates has longer fibers than that from milder climates. It is easy to see that the average breadth of the fibers from warm climates is greater, since the percentage of summerwood is smaller in fast-growing trees than in slow-growing ones.

Similar statements would hold for hardwoods. Here most of the fibers are libriform. The following data may be quoted from Trendelenburg (13).

Kind of Wood	Average Length of Libriform Fibers mm.
Beech	
5 years.....	0.58
45 years.....	1.25
Oak	
2 years.....	0.60
127-130 years	1.22
Beech (140 years)	
1.3 m. from the ground...	1.2
24 m. from the ground....	0.8

The averages are computed from individual values which are widely scattered. This is also true of the breadths of the fibers. The following figures will give a general idea of the situation:

Kind of Wood	Breadth of Fibers, mm.	
	Maximum	Minimum
Conifers		
Spruce.....	0.069	0.025
Pine.....	0.075	0.030
Hardwood		
Aspen.....	0.046	0.020
Birch.....	0.040	0.014

The figures quoted for the length and width of the fibers would give only an incomplete picture if the size of the cell cavity (lumen) and the thickness of the cell walls were not also noted. This question has recently been taken up in various connections (14). Such properties as the stiffness and plasticity of the fibers are very much dependent on these quantities. Fibers with thin walls and large cavities appear like collapsed tubes after isolation by chemical methods, and are therefore called band fibers. On the other hand, the cells with heavy walls and narrow cavities are scarcely affected, and yield hard, stiff tubular fibers. The difference between

springwood and summerwood of conifers is easily seen; the thin-walled cells of springwood give band fibers, and the heavy-walled summerwood cells give rise to tubular fibers.

Further examples may be found among the hardwoods. Figure 25, taken from the work of W. Mühlstepl (14), gives curves showing the distribution of fibers with varying thickness of the cell wall, given in per cents of the total fiber breadth, for four different woods — musanga (*Musanga Smithii*), spruce, aspen, and red beech.

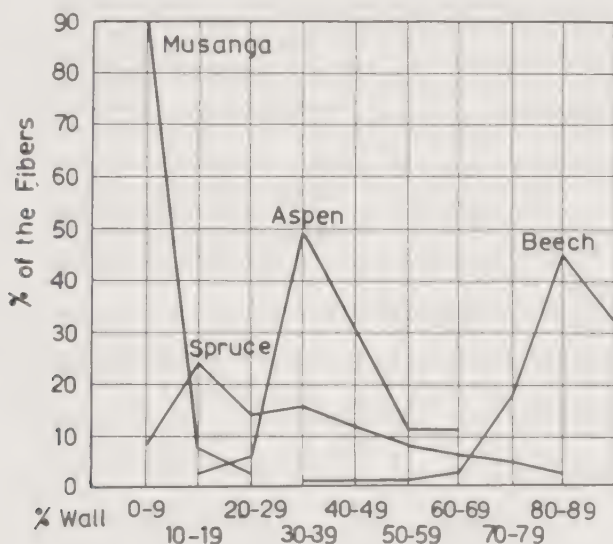


Fig. 25. Percentage of the breadth of the fibers contributed by the fiber wall.

It may be seen that musanga wood contains chiefly thin-walled cells with large cavities, while the beech fibers have thick walls and narrow cavities. The fibers of spruce consist, as has already been pointed out, of a mixture of both kinds, while the fibers of aspen wood lie definitely between the two extremes.

The following values taken from Mühlstepl will indicate the absolute sizes of cavity and cell wall in the fibers of these woods:

Kind of Wood	Density	Dimensions mm. \times 1,000			% of Wall
		Cavity	Wall	Total	
Musanga.....	< 0.35	37.6	2.7	43	12.5
Spruce.....	\sim 0.45	24	6	36	33.3
Aspen.....	0.4-0.6	12.4	4.3	21	41.0
Beech.....	> 0.6	0.6	4.7	10	92.0

This question is of the greatest practical importance, especially for paper making. Thin-walled fibers with large cavities and a large cross-sectional area are plastic, while those with thick walls are less so. The properties of the paper made from the fibers is decisively influenced by

this factor, even when the pulp is not beaten, but especially when it is. This was made very clear by the extensive investigations of R. Runkel (15). It turned out, for example, that sulfate pulps with a tensile strength of about 12-13 km. could be produced from the short-fibered balsa wood (*Ochroma lagopus*). Other short-fibered tropical woods, like *Ceiba pentandra*, also gave papers with a tensile strength of the same order of magnitude when the fibers were beaten to about 50° S.R.; this is just as high as that obtained with good, long-fibered pine wood.

Recently, Th. Wegelius (16) has investigated the variations of the anatomic-structural properties in Finnish spruce wood. Preliminary experiments showed that the yield of cellulose in chemical pulping was greatest when the annual rings were of a normal width. Broad-ringed wood as well as wood of especially poor growth, with narrow rings and a higher content of "compression wood" (cf. following section) yielded somewhat less cellulose. The mechanical characteristics of the pulp were influenced, both by the content of knots, and by the ratio of springwood and summerwood. A high percentage of springwood improved tensile strength and bursting strength, while a high content of summerwood gave good initial tear values.

For the physical and chemical structures of the fiber walls cf. p. 358.

VII. Compression and Tension Wood

A tree trunk which has been pulled out of the vertical tends, because of geotropic stimulation, to resume an upright position. In the case of conifers this is achieved through the influence of hormones which so affect the activity of the cambium that the length and breadth of the new annual rings increases on the underside of the stem. This causes a longitudinal compression, leading to a gradual resumption of the vertical position. The wood which is formed in this way on the underside of the trunk is compact, has a high specific gravity, and is brown in color. It is known as "compression wood."

In the case of hardwoods, under the same circumstances, the activity of the cambium is so regulated that a *shortening* of the annual rings on the *upper* side of the stem results. The wood so formed is known as tension wood, or, because of its color, as "white wood." Similar adjustments can occur in the branches. Compression and tension woods together are known as "reaction wood."

The tracheids of compression wood are shorter than those of normal wood. They are also considerably broader, and are so rounded that they leave large intercellular spaces in the wood.

The outermost (primary) thickening of the cell wall consists of a highly lignified layer, composed of spiral bands. The secondary wall is also lignified, and much thickened. It is composed of a large number of spiral bands connected together. There is no tertiary wall (Fig. 26).

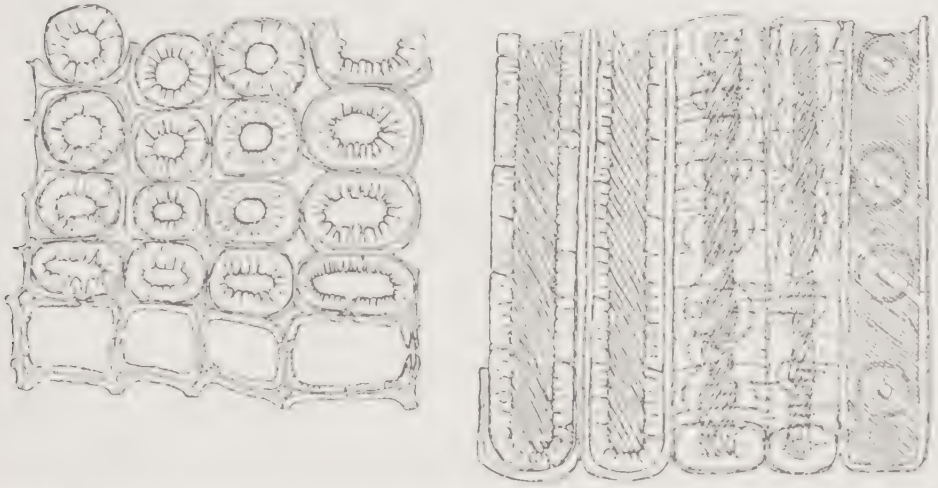


Fig. 26. Compression wood (spruce). Left, transverse section, right, longitudinal section.

A "white wood" is found on the upper side of the spruce branch; its tracheids consist of a strongly lignified primary layer, a less lignified secondary layer, and a very thick and very much lignified tertiary layer.

It may be said that ordinary wood, which is exposed alternately to tension and compression, constitutes a transitional form between compression wood and tension wood.

No compression wood appears to be present in hardwoods. The tension wood present shows a fundamental difference from that of conifers. Besides the lignified primary and secondary layers, there is also an unlignified very broad tertiary layer. According to G. Jayme and M. Harders-Steinhäuser (18), this pure polysaccharide layer, in contrast to the lignified layers, gives a strong violet color reaction with zinc chloride-iodine solution. The specific gravity of the tension wood of *Populus canadensis* was shown to be 17.48 per cent higher than that of normal wood. The tension wood contained less lignin, pentosans, and easily soluble hemicelluloses—but more cellulose—than the normal wood.

The strength of the reaction woods can not, according to E. Münch (17) be attributed entirely to the extensive lignification of the fibers, but depends upon the layered and spiral construction of the cell walls. A great similarity may be observed to the structure of animal bones, which also consist of numerous layers of fibrils with the same helical arrangement.

The primary layer of the tracheids of compression wood is, as has been remarked, spiral in form. The pitch is small, so that the layer almost appears to be cross-striated. The secondary layer is also helical, but the pitch is here considerably greater. When the compression wood is subjected to longitudinal compression, the spirals of the secondary layer are spread out sideways, but the primary layer, which because of its smaller pitch can not spread out so far, prevents the further spreading of the secondary layer, and hence prevents the entire fiber from being further broadened and shortened. Thus the whole fiber becomes stiffer and less flexible. In normal wood the spirals of the secondary layer in the tracheids seem in general to have a smaller pitch than in compression wood. It follows that normal wood must be more resistant toward compressive stresses than is compression wood; this is manifested in the higher modulus of elasticity of normal wood.

It is not wholly clear just how the compression wood accomplishes the erection of the trunk into a vertical position. It is supposed that a great role is played by the laying down of new micelles; this results in a thickening of the spiral layers, and hence in a longitudinal pressure.

The white wood of the branches of coniferous wood contains tracheids all of whose layers are spiral-shaped. The pitch is variable, but is usually quite large. When such tracheids are subjected to lengthwise tension, the outermost spiral is pulled out, causing a pressure on the inner, flatter spiral. This contains that component of the force which is directed toward the inside. The extensively lignified tertiary layer is also effective in this respect. The white wood of conifers appears to play a chiefly static rôle, but that of deciduous trees has a dynamic purpose, too, namely the elevation of a trunk which has been displaced from its vertical position. The different structures of the two white woods may be explained on this basis. In the hardwoods the broad, tertiary layer is fibrillated in a direction almost parallel to the axis. According to Münch (17), the active shortening of the rings might be due to an irreversible swelling of this layer. This would exert a pressure upon the outer, spiral-shaped layers, causing a decrease in the pitch of the spirals. This would result in a shortening of the cell. Other explanations are possible.

The reason for the spiral form of the cell walls, according to Münch (17), would be to convert longitudinal stresses into transverse stresses, and transverse stresses into longitudinal ones.

REFERENCES

1. Dengler, A., in Mahlke-Troschel, *Handbuch der Holzkonservierung*, 2nd edition, Berlin, 1928, p. 1.
2. Johnston, H. W., and Maass, O., summarized in Kollmann, F., *Technologie des Holzes*, Berlin, 1936, p. 9.
3. Fabricius, L., quoted by Trendelenburg, R., *Das Holz als Rohstoff*, Berlin, and Munich, 1939, p. 113.
4. Huber, B., and Prütz, G., *Holz Roh- u. Werkstoff* **1**, 377 (1938); cf. Trendelenburg, R., Ref. 3, p. 83, 85, and Kollmann, F., Ref. 2, p. 18.
5. Kögl, F., *Angew. Chem.* **46**, 469 (1933); *Svensk Kem. Tid.* **43**, 145 (1936).
6. Eneroth, O., in *Handbok i Skogsteknologi*, Stockholm, 1920, p. 25.
7. Hägglund, E., *Svensk Papperstidn.* **38**, 454 (1935).
8. Sachs, J., *Vorlesungen über Pflanzenphysiologie*, 1882, p. 138.
9. Anderson, E., and Pigman, W. W., *Science* **105**, 601, (1947).
10. Trendelenburg, R., *Das Holz als Rohstoff*, Berlin, 1939, p. 72.
11. From Lee, H. N., *The Manufacture of Pulp and Paper*, III, New York, 1927, p. 29.
12. Hägglund, E., *Svensk Papperstidn.* **37**, 133 (1934); **38**, 454 (1935).
13. Trendelenburg, R., *Das Holz als Rohstoff*, Berlin, 1939, p. 76.
14. Cf. Ritter, G. J., *Paper Trade J.* **101**, No. 18, 92 (1935); Potter, G. J. C., and Yorstson, F. H., *Pulp Paper Mag. Can.* **38**, 103 (1937); Runkel, R., *Wochbl. Papierfabrik.* **71**, 93 (1940); *Zellstoff u. Papier* **21**, 139 (1941); Muhlsteph, W., *Wochbl. Papierfabrik.* **72**, 201, 219 (1941).
15. Runkel, R., *Wochbl. Papierfabrik.* **71**, 93 (1940).
16. Wegelius, T., *Svensk Papperstidn.* **49**, 51 (1946).
17. For an extensive discussion, see Münch, E., *Flora* **132**, 357-424 (1938).
18. Jayme, G., and Harders-Steinhäuser, M., *Papier* **4**, 104 (1950).

CHAPTER II

THE PHYSICAL PROPERTIES OF WOOD

I. The Specific Gravity

The main factor influencing the specific gravity of wood —the weight in grams of 1 cc. of absolutely dry wood —is the ratio between the volume of the pores and the volume occupied by the cell walls (or the compactness of the body of the wood). The specific gravity of the actual woody substance is less important; it is practically constant, and equal to 1.5, at least in those woods which are most frequently dealt with in practice, as, for example, in the making of pulp. Let us use the following notation:

- a = specific gravity of the wood
- b = volume of pores per unit volume
- c = specific gravity of actual woody substance

Then the relationship holds:

$$b = 1 - a/c$$

or in percentages

$$b = 100 (1 - a/c) = 100 (1 - a/1.5) = 100 (1 - 0.67 a)$$

If the specific gravity of the dry wood is known, the relationship between the volume of the cell walls and that of the pores can be calculated from these formulas. The following table gives the result of such calculations:

Specific Gravity	Volume Percentages	
	Cell Walls	Pores
0.3	20	80
0.4	27	73
0.5	34	66
0.6	40	60
0.7	47	53

The volume of the pores is not constant, as has already been implied, but varies with the relative amounts of springwood and summerwood, as may be seen from the following figures:

Type of Wood	Breadth in mm.	Annual Rings	Specific Gravity of Absolutely Dry Wood
		% of Summerwood	
Spruce.....	{ 0.8	20-25	0.48
	{ 2.0	15	0.43
	{ 3.4	< 10	0.40
Pine.....	{ 1.3	30	0.54
	{ 0.75	15	0.43
	{ 5.5	< 10	0.42

The following factors by influencing the pore volume thus affect the specific gravity of the wood: the percentage of summerwood, the breadth of the annual rings, and the relative thickness of the cell walls. These factors are in turn dependent on the kind of wood, the age of the tree, the place where the tree was grown, and even the position of the tree in the stand from which it came. The part of the trunk from which the wood was cut also has an effect. So far as the type of tree is concerned, hardwoods are usually denser than softwoods, but the specific gravity of the same type of wood is not always the same. Indeed it is so widely variable that no sharp distinctions can be drawn between the different kinds of woods. This may be seen from the following table where the average specific gravities and the range of variation are given for various European woods.

Type of Wood	Specific Gravity	
	Range	Average Value
Spruce.....	0.31-0.55	0.43
Pine.....	0.31-0.70	0.52
Larch.....	0.41-0.70	0.57
Birch.....	0.51-0.75	0.60
Beech.....	0.56-0.76	0.70
Oak.....	0.46-0.85	0.68

It is seen that the specific gravity is extremely variable; R. Trendelenburg (1) has determined frequency curves for various woods, such as white pine (*Pinus strobus*), spruce, pine, larch, oak, and beech. These curves are given in Fig. 27.

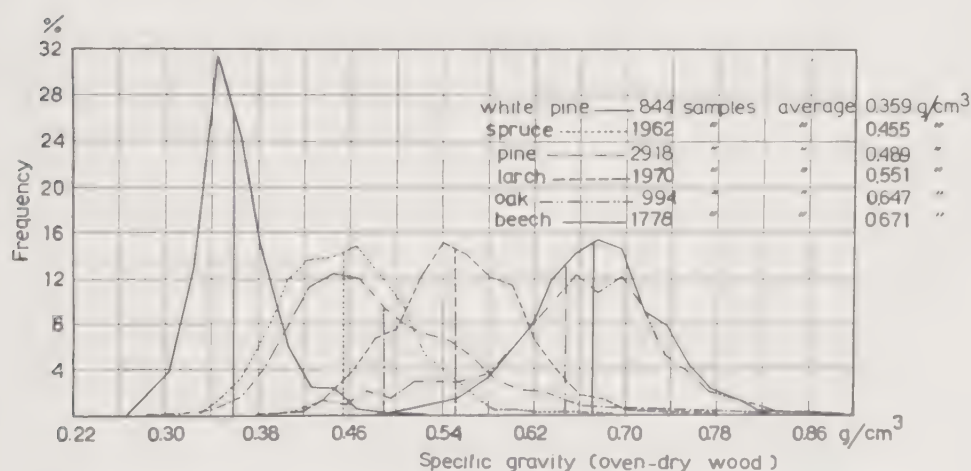


Fig. 27. Frequency curves of specific gravities for various kinds of woods.

Other physical properties, such as the compressive strength, depend on the specific gravity; dense wood has a high compressive strength, and lighter wood has less. The specific gravity varies considerably, even

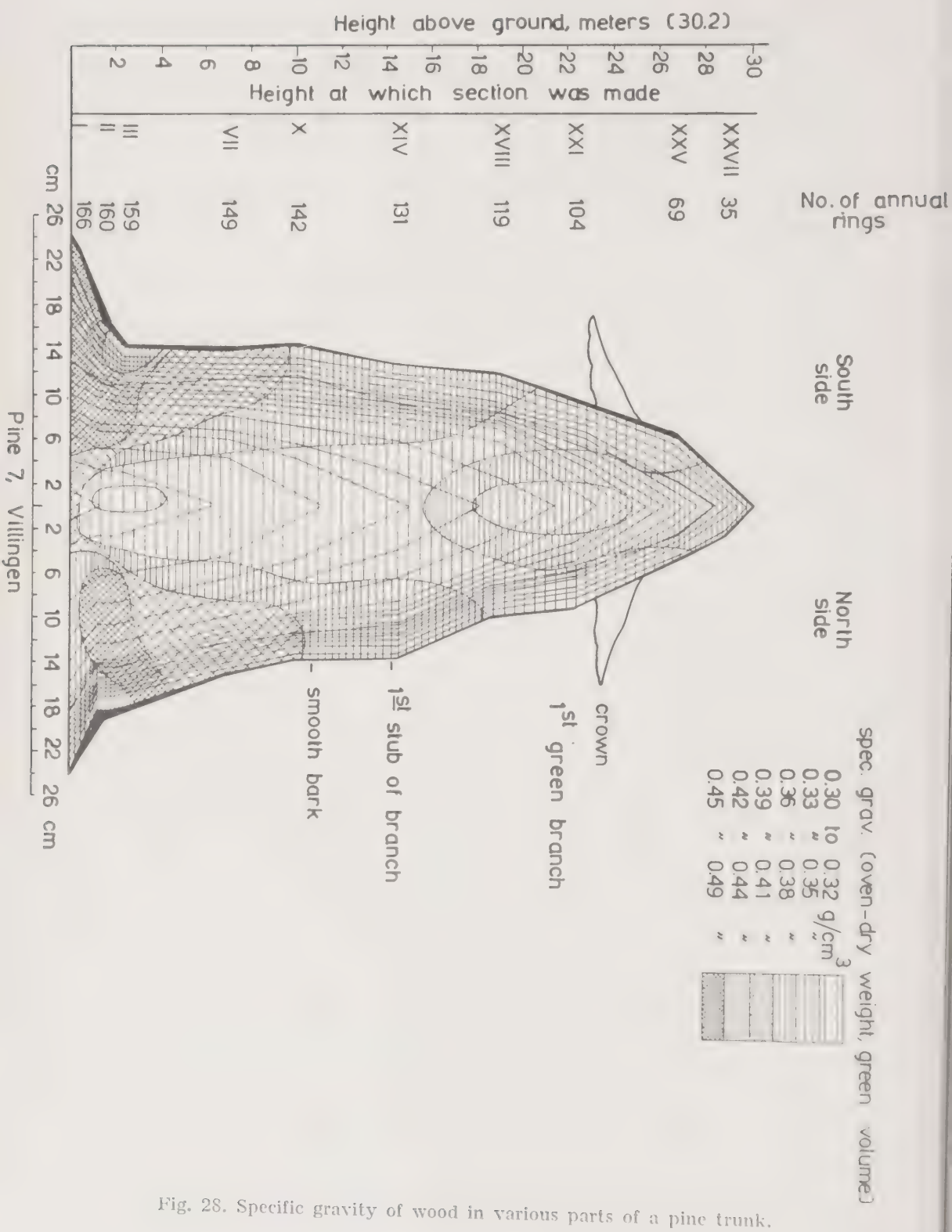


Fig. 28. Specific gravity of wood in various parts of a pine trunk.

within the same tree, as Trendelenburg (1) has shown. This is illustrated in the schematic diagram (Fig. 28) of the specific gravity of the wood in various parts of a pine trunk.

It has been mentioned that the specific gravity of the woody material is about 1.5 (2). Since this is made up primarily of carbohydrates of high molecular weight (particularly cellulose) and of lignin, it is interesting to inquire how the cellulose and the lignin influence the density of the wood. The figures quoted in the literature for the specific gravity of native cellulose as well as for wood cellulose and for cotton cellulose range from 1.52 to 1.60. If these figures are correct, the lignin should be somewhat lighter than the wood. According to A. J. Stamm and L. A. Hansen (2) the specific gravity of lignin is about 1.4. The conclusion may be drawn that variations in the lignin contents of various woods do not appreciably influence the specific gravities of their woody substance.

II. The Water Content

A. WATER CONTENT OF THE WOOD OF LIVING TREES

The water content of the wood of growing trees or of so-called "green wood" depends primarily upon the structure of the wood, and most particularly upon the volume of the pores. The more compact the wood, the less is its water content. The mechanically enclosed water is found chiefly

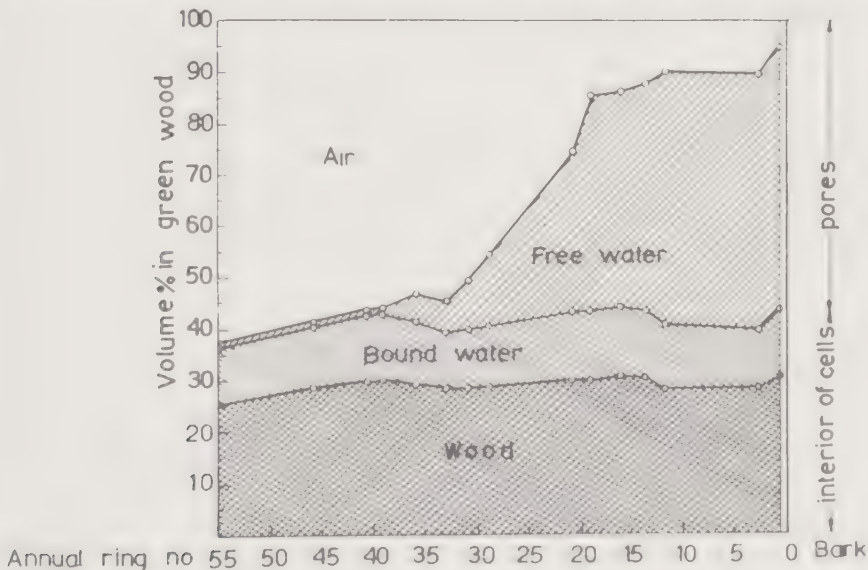


Fig. 29. Variation in the volume per cent of wood, water, and air in the outer 55 annual rings of a spruce tree felled in the middle of July in the Tharand forest. (Section taken 1 meter above the ground.) Drawn from data calculated from the experiments of Langner (3).

in the pores of the sapwood. Only a little water is enclosed in the heartwood, the amount again being less, the more compact the wood.

These facts stand forth very clearly in Fig. 29, taken from the often-quoted book of Trendelenburg (2, 3). It is seen that the wood in the outermost annual rings is completely filled with water during the growing season; this is indeed natural, for such a condition is probably a prerequisite for the rising of the sap. In the innermost annual rings—the heartwood—there is practically no “free” water in this case. These variations in water content have a great influence on the specific gravities of the various parts of the wood. [For further details see R. Trendelenburg (2), p. 214 ff.].

B. WATER CONTENT OF AIR-DRIED WOOD

When a piece of green wood is dried in the air, the water escapes until a certain degree of dryness is reached. The resulting product is known as “air-dried” wood. The water content of such wood depends upon the relative humidity of the air, and upon the temperature; *i.e.*, an equilibrium is established, as may be seen from Fig. 30.

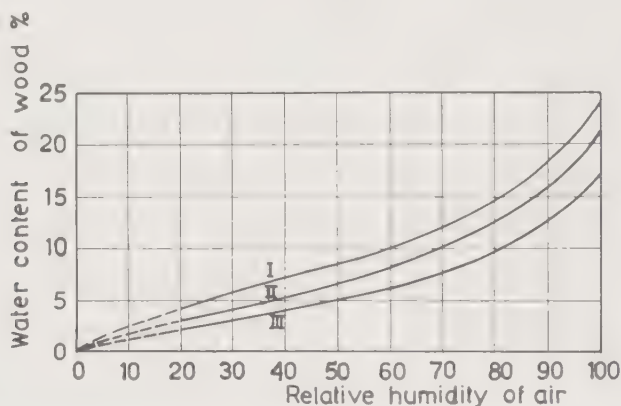


Fig. 30. Relationship between water content of air-dry wood and humidity of the air at various temperatures.

I = 21 °C., II = 61 °C., III = 100 °C.

Curve I represents the equilibrium at 21° C. (70° F.); curve II, that at 61° C. (142° F.); and curve III, that at 100° C. (212° F.). At between 20 % and 50 % relative humidity the curves are nearly straight; *i.e.*, the water content of the wood is a linear function of the relative humidity. The relative humidity of the air varies with the season of the year. The conditions for Northern Sweden (latitude about 65°) are represented in Fig. 31.

The speed of drying depends very much upon whether or not the bark is left on, for the bark of freshly felled trees hinders the evaporation of

water. It has been found that trees felled in the winter do most of their drying the following spring. Trunks which have had all their bark removed

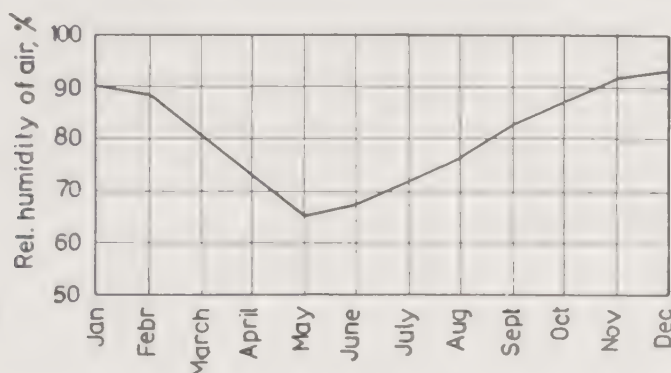


Fig. 31. Relative humidity of the air at various seasons in Sweden (average values).

dry fastest (Fig. 32). In three months of the spring (in Sweden) they become completely air-dry. This is not the case with partly peeled trees. Trunks with the bark on dry only very slightly in the first year, but since most of the bark falls off during the second year, the drying then proceeds rapidly. These remarks apply to softwood.

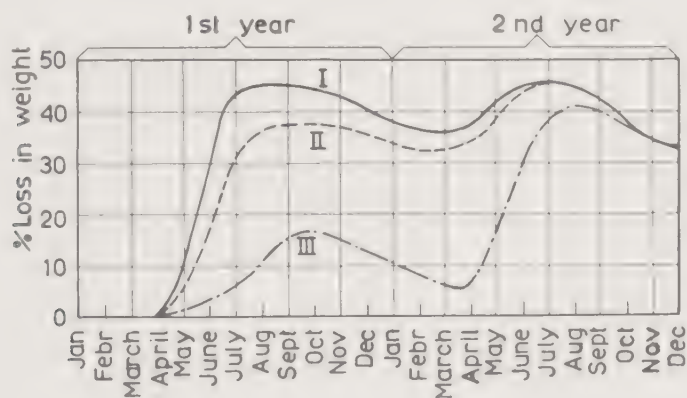


Fig. 32. Speed of drying of green trunkwood.

I—Bark removed II—Bark partially removed III—Bark not removed.

Thin trunks naturally dry faster than thicker ones, as the following table shows:

Average Diameter of Trunk (cm.)	Period Since Felling (Years)	% Content of Water	
		Spruce	Pine
Less than 5.5...	{ 1	18.5	22.7
	{ 5	17.5	19.9
Greater than 5.5.	{ 1	22.1	35.8
	{ 5	18.8	29.0

The speed of drying of hardwood trunks from which the bark has not been removed can be accelerated considerably by leaving the crown attached. This fact, which is of great practical importance, may be illustrated by the following example. R. D. Gibbs (4) found that the water content of the trunk of Canadian birch decreased from about 90 % to 50 % in the period from June to September, when the bark and crown were left on, whereas a section of trunk 1.2 m. long from which the crown had been removed still contained 74 % of water after the same period of drying. If the bark was removed from the section of the trunk (which had no crown attached) the water content decreased to 43 % in the same length of time.

III. The Relation between Specific Gravity and Water Content

The connection between the specific gravity and the water content may be seen from Fig. 33. The curves b' and a' represent the specific gravities of two different kinds of wood. Above a water content of 30 %, the specific gravity is a linear function of the water content.

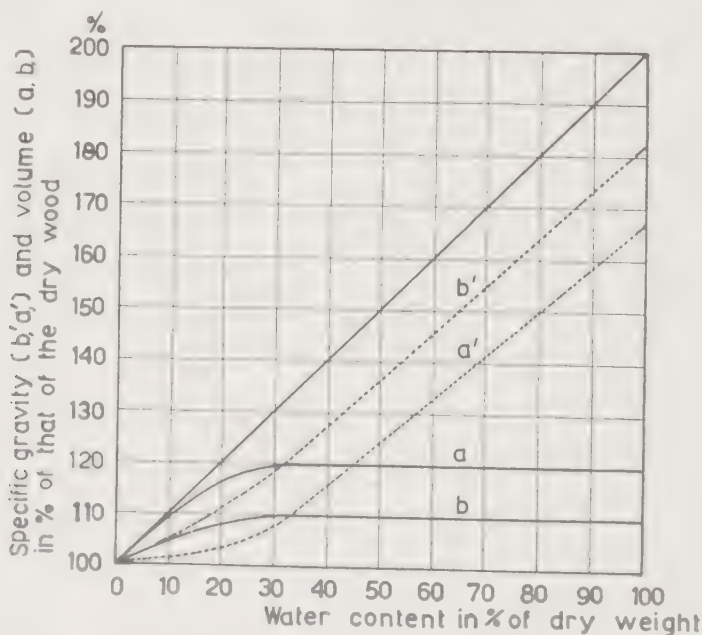


Fig. 33. The specific gravity (----) and volume (—) as a function of the water content of the wood.

a , for large shrinkage on drying; b , for small shrinkage on drying. The total weight of wood plus water is given by the 45° line.

The shrinkage of the wood may also be discussed in this connection. As may be seen from curves a and b , the volume remains constant when

the moisture content is greater than 30 %. When moist wood is dried, the volume is not affected as long as the water is being removed only from the interior of the cells and the intercellular spaces. But as soon as the water so contained is exhausted, a shrinking of the cells begins, which leads to a change in volume. The water content at which the shrinkage begins is known as the saturation point of the fibers. This is at about 25-30 % of the dry weight in most types of woods.

The extent of shrinkage varies with the type of wood; light, porous woods shrink less than dense, compact ones. This may be seen from the following table, which gives the decrease in volume when 10 % of water is lost; the shrinkage is expressed as a percentage of the volume of the absolutely dry wood.

Kind of Wood	Specific Gravity of Absolutely Dry Wood	Moisture Content of Air-Dry Wood, in % of Weight of Absolutely Dry Wood	Contraction on Loss of 10 % of Water in % of Volume of Absolutely Dry Wood
Spruce.....	0.412	13.7	4.9
Pine.....	0.494	13.6	4.3
Larch.....	0.566	13.6	5.5
Aspen.....	0.425	14.1	4.1
Birch.....	0.679	15.1	5.1
Beech.....	0.700	13.6	5.9

Since the water content of air-dry wood is less than that corresponding to the saturation point of the fibers, air drying results in a decrease in volume which averages half of the total decrease in volume caused by complete drying. This may be seen from the following table:

Kind of Wood	Contraction in % of the Volume of the Green Wood	
	From Green Wood to Air-Dry Wood (12-15 % Water Content)	From Green Wood to Absolute Dryness
Spruce.....	7.4	14.8
Pine.....	5.8	11.5
Birch.....	8.4	16.8
Beech.....	8.0	16.1
Oak.....	7.8	15.7

As has already been said, the specific gravity of the wood depends primarily on the structure of the wood and therefore also on the relative amounts of heartwood and sapwood which are present. It can, therefore, vary considerably. The following average values may be given for various kinds of wood, in the green, air-dry, and completely dry conditions (5).

Kind of Wood	Green	Air-Dry	Absolutely Dry
Spruce.....	0.80	0.47	0.41
Pine.....	0.90	0.52	0.49
Larch.....	0.76	0.60	0.56
Aspen.....	0.80	0.47	0.43
Birch.....	0.95	—	0.68
Beech.....	0.99	0.74	0.70

The specific gravity of a wood is the weight of a unit volume of the fully dried (and hence, shrunken) wood. It is often of practical value, however, to know what weight of water-free wood is contained in a unit volume of the uncontracted wood. The following figures may be quoted [R. Trendelenburg (2), p. 211]:

Kind of Wood	Specific Gravity g./cc.	Content of Water- Free Wood in Uncontracted Wood g./cc.	Saturation Point of the Fibers in %
Pine (heartwood).....	0.472	0.420	27
Spruce.....	0.442	0.390	31
White pine (heartwood).....	0.345	0.320	24
Beech.....	0.678	0.560	32

The swelling of wood when it takes up water is due to expansion of the cell walls caused by the entrance of water into the small interspaces within the wall and by the absorption of water by the cellulose chains or micelles. The swelling is, however, limited; this leads one to the conclusion that the chains are held together by lateral bonds which are not broken by the action of water. Such networks occur in the case of other high-polymeric substances, and there, too, the addition of solvents (6) causes a limited increase in volume.

H. Saechtling and H. Zocher (7) have investigated the swelling of spruce in various solvents, such as benzine, ether, acetone, pyridine, methanol, and water. Pyridine had a specific effect. For the other solvents, the swelling increased in the order in which the solvents are named.

For further information concerning the swelling and drying as well as other physical properties of wood—mechanical, thermal, electrical, and acoustical properties—the reader is referred to books especially dealing with these subjects, as F. Kollmann, *Technologie des Holzes*, Berlin, 1951; H. E. Desch, *Timber, its Structure and Properties*, London, 1947; and to the excellent articles by C. C. Forsaith, *The Physical Properties of Wood*, and A. J. Stamm, *Surface Properties of Cellulosic Materials*, in L. E. Wise, *Wood Chemistry*, New York, 1946.

REFERENCES

1. Trendelenburg, R., *Das Bayerland* **47**, 513 (1936).
2. Stamm, A. J. and Hansen, L. A., *J. Phys. Chem.* **41**, 1008 (1937); Trendelenburg, R., *Das Holz als Rohstoff*, Berlin, 1939, p. 189.
3. Cf. also Langner, W., *Botan. Arch.* **34**, 1 (1932).
4. Gibbs, R. D., *Can. J. Research* **12**, 727 (1935).
5. Eneroth, O., in *Handbok i Skogsteknologi*, Stockholm, 1920.
6. Cf. Staudinger, *Angew. Chem.* **49**, 801 (1936). For the network formation with cellulose chains, see also p. 48-49.
7. Saechtling, H., and Zocher, H., *Kolloid-Beihfte*, **40**, 411 (1934).

CHAPTER III

THE WOOD COMPONENTS AND THEIR CHEMICAL PROPERTIES

The first reliable data on the elementary composition of wood were given by E. Gottlieb (1). He reported the following figures for the woods mentioned below; these are averages of many values, which usually were in good agreement.

Kind of Wood	C	H	N	Ash
Oak.....	50.16	6.02	—	0.37
Ash.....	49.18	6.27	—	0.57
Hornbeam (<i>Carpinus betulus</i>)	48.99	6.20	—	0.50
Beech.....	49.01	6.11	0.09	0.54
Birch.....	48.88	6.06	0.10	0.29
Fir.....	50.36	5.92	0.05	0.28
Spruce.....	50.31	6.20	0.04	0.37

W. Daube (2) investigated the elementary composition and the ash content of sapwood and heartwood, with the following results:

	103-Year-Old Larch		104-Year-Old Pine		75-Year-Old Spruce		125-Year-Old Oak		180-Year-Old Beech	
	Sap- wood	Heart- wood	Sap- wood	Heart- wood	Sap- wood	Heart- wood	Sap- wood	Heart- wood	Sap- wood	Heart- wood
C....	49.57	49.86	50.18	54.38	50.03	49.55	49.15	50.28	48.92	49.06
H....	5.85	5.91	6.08	6.31	6.05	6.18	5.84	5.62	5.86	5.91
N....	0.17	0.12	0.17	—	0.19	0.18	0.35	0.28	0.24	0.22
Ash..	0.22	0.12	0.19	0.15	0.26	0.20	0.42	0.16	0.47	0.40

The analyses for carbon show good agreement between sap- and heartwood, except in the case of pine. This is understandable, since the high content of resin markedly influences the value for carbon. The great differences in the compositions of various kinds of woods are not revealed by their elementary compositions.

I. The Components of the Woody Substance

A. HISTORY

The question of the chemical constitution of the woody substance has been the subject of repeated investigations for the past hundred years. H. Braconnot (3) had early discovered that the action of strong sulfuric acid on white-beech wood results in the formation of large quantities of soluble carbohydrates. From 16 g. of beech sawdust he obtained 5 g. of

residue, insoluble in sulfuric acid, and 10 g. of gummy substances. The conclusion was drawn that considerable quantities of carbohydrate must be present in the woody substance. At this time it was assumed that wood was a uniform substance (4).

A deeper insight into the composition and nature of the cell walls came only with the fundamental studies of A. Payen (5). He treated various woods with nitric acid, alkalies, alcohol, and ether successively, and found that the residues had the formula $C_6H_{10}O_5$; they were therefore isomeric with starch. Payen regarded the residues from all his preparations as identical with *cellulose*. His treatment caused a material to go into solution which had a higher carbon content, and which he designated as an "incrusting substance."

A characteristic color reaction for cellulose was discovered at about the same time. M. J. Schleiden (6) observed that cellulose was colored blue by 66 % sulfuric acid containing 1 % iodine. It was found that cellulose isolated by the procedure of Payen showed this reaction, while wood itself did not. Payen explained this on the assumption that the cellulose was mechanically enclosed in the substance which made up the cell walls. He did not believe that the two substances were chemically combined, but rather, as has been stated, that this was a true case of "incrustation."

This question was much discussed in the following years, and has not yet been completely settled. J. Erdmann (7) was of the opinion that wood should not be regarded as a heterogeneous mixture, but rather as a chemical compound between the cellulose and the other constituents of the cell wall; F. Bente (8) had similar ideas. At about the same time (1857) there appeared a study by F. Schulze (9) who treated wood with potassium chlorate and nitric acid, and obtained a residue which he regarded as pure cellulose. (We shall see later that cellulose can not be determined in this manner). He believed that the cellulose was the substance in the cell walls which really determined the structure, and that when the incrusting material had been removed by oxidizing agents the shape and dimensions of the structural elements were not changed. According to this view, the "lignification" came about through incrustation by *lignin*. F. Schulze was the first to call the incrusting material by this name. The "lignin" of Schulze is not identical with what we now know as lignin, for it included about 50 % of the woody substance, or all the material which went into solution on long-continued treatment with potassium chlorate and nitric acid. A gross formula was also calculated for this material, but Schulze understood clearly that nothing definite could be said about its composition until a method for isolating it had been discovered. Schulze reported

one method for isolating lignin by means of strong sulfuric acid, but he believed that this did not give a pure product, since it turned black and yielded humus-like substances.

J. Erdmann had the idea that the woody substance was a chemical compound of uniform composition, and termed it "glycolignose." This he supposed to contain a *sugar-forming group*, an *aromatic group*, and a group of "*primitive cellulose*." Similar views were held by E. Fremy (10) who made extensive analyses of woody substances. According to Fremy, there were three fundamentally different components: 1. "cuticle ligneuse" 2. "substance incrustante" 3. "substance cellulosique." The first of these corresponded in general to the present-day lignin, the second to hemicellulose or wood polyoses which still contain some lignin, and the third to cellulose or to cellulose and related carbohydrates. Fremy found, for example, 20 % of 1, 40 % of 2, and 40 % of 3 in beech wood. In his opinion there were various kinds of cellulose in wood, which he called "cellulose," "paracellulose," and "metacellulose," etc. He rejected Payen's incrustation hypothesis.

Further studies of the sugars obtained by hydrolysis showed that there might be several "celluloses" present in the cell walls (11). A. Muntz (12) and later E. Schulze and his co-workers (13) found galactose in the hydrolysis products, and F. Koch (14) further established the fact that the so-called wood gum of T. Thomsen (15) contained the hitherto unknown polysaccharide *xylan*. It had already been proved that hydrolytic decomposition of plant membranes gave rise to mannose (16).

All of these polysaccharides were distinguished from the other constituents of the cell walls by the fact that they were easily hydrolyzed by dilute acids. E. Schulze (17) first introduced the name "*hemicellulose*" as a generic term for these constituents; the individual substances were called galactan, xylan, etc. The term "cellulose" was reserved for those substances which were not appreciably attacked by dilute mineral acids and alkalies, nor by the reagent of F. Schulze. Cellulose was shown to be soluble in ammoniacal copper solution; on hydrolysis it yielded grape sugar (D-glucose).

E. Schulze had already made earlier attempts to classify the carbohydrates present in the various substances of the cell walls. He thought it would be convenient to designate some of them as "reserve celluloses," and others as "skeletal celluloses." The former had the function, as the name indicates, of serving as reserve materials for future metabolic processes, while the latter were essentially present to give mechanical strength to the woody tissue.

This division along physiological lines is to a large extent still retained.

It is important to bear in mind, however, that in most plant membranes and also in wood it is difficult to draw the line between skeletal and reserve materials (18). This question will not be further discussed, since reserve substances do not occur in wood to any great extent, except in unusual cases.

Of more importance is the question as to whether the term "hemicellulose" should be retained. The expression derived, as has been noted above, from a time when the hemicellulose was usually regarded as a sort of intermediate stage in the formation of cellulose.¹

Such a concept is not in agreement with the present-day knowledge of cellulose. The definition of hemicelluloses as the easily hydrolyzable carbohydrate components is no longer suitable, either; among the hemicelluloses there are some compounds which obviously can not be sharply separated from cellulose by hydrolysis.

K. Hess (18) has suggested that the generic term hemicellulose be abandoned, and that it be replaced by the designation "attendant carbohydrates." This term has, however, not yet won general acceptance, perhaps because it does not rule out confusion with other groups of carbohydrates.

P. Klason (23) has made another suggestion, namely, that the carbohydrates which accompany the cellulose be called "lignosans." This proposal did not become generally known, however, and hence was not taken up.

H. Staudinger (24) has given to these carbohydrates the name "*wood polyoses*." The term hemicellulose has often been extended in technical usage to include all alkali-soluble constituents of wood pulp;

¹ K. Hess, W. Wergin, C. Trogus, and J. Gundermann (19) have reported interesting observations on the formation of cellulose in plant fibers. They found that no cellulose was visible in the X-ray pattern of a cotton hair until the 35th day of development. Only the pattern of a "primary substance" is obtained; this is different from cellulose. Hess and his co-workers conclude that for the first 35 days growth occurs in length only, and that only thereafter does thickening take place, accompanied by the deposition of layers of cellulose on the inside. Oddly enough, the "primary substance" is said not to consist of carbohydrates, but to be more wax-like. K. Hess and W. Engel (20) later found that besides the wax, pectins are also present. When the hair is 10 days old the "primary pectin" constitutes no less than 35 % of the hair wall. The amount of pectin decreases after this, and drops sharply when the fiber matures. According to these observations, the primary wax and primary pectin would have a close connection with the formation of the cell wall. According to W. Farr (21) the cell wall of cotton and other plants consists of cellulose embedded in a cementing mass of pectin-like material. E. Heuser, and J. W. Green (22) subjected cotton to the longcontinued action of ammonium oxalate. The material was physically unaffected. Material so treated, or merely de-waxed, was dissolved in ammoniacal copper solutions, the viscosity measured, and the molecular weight determined by Staudinger's method. The molecular weight turned out to be 488,000; with extracted samples it was about 25 % lower, but when the samples had been handled in an atmosphere of nitrogen, it was only 12-17 % less. These results show that the cotton fibers dissolve as a whole in cuprammonium solutions, and that Farr's cementing substance is improbable as a major constituent of the fibers.

this could of course lead to errors, since degraded cellulose is also soluble in sodium hydroxide. The woody substance doubtless also contains, in addition to the polyoses, small amounts of substances which on hydrolysis yield various types of uronic acids. Since these substances are not, strictly-speaking, polyoses it seems proper to designate them as *polyuronic acids*.

The investigations discussed above have caused the meaning of the term "lignin" to become steadily narrower. Berzelius called the whole of the wood lignin; F. Schulze understood by lignin only that part of the wood which went into solution on oxidation with potassium chlorate and nitric acid, and even gave an empirical formula for it; finally the work of E. Schulze led to recognition of the fact that this part included a number of carbohydrates. P. Klason (23) calculated from the difference in weight between the wood and the cellulose, including wood polyoses and accessory constituents, that the lignin in spruce wood amounted to 30 %, which is in satisfactory agreement with the true value. Klason later gave a method for determining lignin with 70 % sulfuric acid.

It is known, then, that wood is composed of the following chief constituents: cellulose, carbohydrates which accompany the cellulose and include wood polyoses and polyuronic acids, and a less-known material with a high carbon content, which is called lignin.

This classification will be retained in the detailed discussion of the composition of wood which follows.

II. Cellulose

A. THE STRUCTURE OF CELLULOSE

B. Tollens (25) in the 3rd edition of his well-known "Kurzes Handbuch der Kohlenhydrate" characterizes cellulose as a substance occurring in the cell walls of plants, whose composition is expressed by the formula $(C_6H_{10}O_5)_n$, and which is not attacked by dilute alkalis or acids, or by potassium chlorate and hydrochloric acid (*i.e.* chlorine) (F. Schulze's reagent). He also reports that cellulose dissolves in strong sulfuric acid and that glucose can be isolated from the solution after dilution and heating. The solubility of cellulose in Schweizer's reagent and in zinc chloride and hydrochloric acid is further noted, as well as the blue color given with iodine and sulfuric acid or with iodine and zinc chloride.

Tollens concludes by saying "cellulose is therefore a polymerized anhydride of D-glucose, which is distinguished by its difficult solubility."

Tollens supposed that a "quite high number" of glucose residues were linked to form a chain, the ends of which were joined to form a huge ring. Other investigators also had ideas similar to those of Tollens. Böeseken (26) for example, in a little-known work to which Freudenberg (27) has recently called attention, concluded from the behavior of cellulose on acetylation with acetic anhydride and sulfuric acid that it was a very large molecule built up of glucose groups. Unlike Tollens, however, he considered it to consist of open chains. At that stage of the development of the science, Tollens might have recorded one other important point — the formation of cellobiose on acetolytic degradation of cellulose.

A quarter of a century earlier A. P. N. Franchimont (28) had obtained on acetolysis of cellulose an acetyl derivative which Z. H. Skraup (29) later saponified with alkali and showed to be an acetate of a disaccharide. The disaccharide was at first called cellose, but later it was designated as *cellobiose*. A whole series of investigators have studied this sugar and its preparation (30). The saponification of cellobiose octaacetate was improved by G. Zemplén (31) as well as by F. C. Peterson and C. C. Spencer (32). The free cellobiose reduces Fehling's solution and yields two molecules of glucose on acid hydrolysis.

Several investigators studied the question of the maximum possible yield of cellobiose which could be obtained. H. Ost (33) succeeded in obtaining 37.2 % and J. Madsen (34), working in Ost's laboratory, was able to raise this to 43 %. K. Freudenberg (35) and P. Karrer and F. Widmer (36) discovered simultaneously that considerable amounts of cellobiose are lost during the acetolysis; it was calculated on the basis of Freudenberg's experiments that something more than 61 % of cellobiose is formed, of which about a third is decomposed. This work undoubtedly constituted the first attempt of fundamental importance to look upon cellulose as a substance made up of a continuous chain of cellobiose residues. Freudenberg pointed out that according to the law of probability one could never expect to obtain a 100 % yield of cellobiose from the acetolytic splitting. He said, "a calculation carried out for me by a friend (37) shows that the decomposition of a uniform polysaccharide chain of 10 or more links in a homogeneous solution would give at most 32 % in the form of disaccharide. If, on the other hand, all the disaccharide formed in all stages of the process crystallized out and a complete yield was thus obtained, 67 % of biose would result. In the case of cellulose, only a part of the disaccharide formed during the reaction crystallized out. The yield actually obtained must, then, lie between 32 % and 67 %, always assuming a uniform chain. Actually 40 % of the theoretical quantity of octaacetylcellobiose was found, and correction for the calculated loss brings the

value near to 67 %. This finding does not, it is true, prove that a continuous cellobiose chain is present, but it certainly does not provide any evidence to the contrary."

The acetolytic breakdown of cellulose (cotton linters) has recently been studied again by S. N. Danilow and P. T. Pastuchow (38). By using hydrochloric acid instead of the sulfuric acid commonly used cellobiose octaacetate could be isolated in yields corresponding to 46-55 % of the theoretical amount.

Important contributions to the further development of the problem of the constitution of cellulose were the studies of the methylation of cellulose carried out by W. S. Denham and H. Woodhouse (39), W. N. Haworth and C. G. Leitch (40), and J. C. Irvine and E. L. Hirst (41). Exhaustive methylation of cellulose and hydrolysis of the methylated product yielded large quantities only of 2,3,6-trimethylglucose. The glucose residues in the cellulose molecule were therefore joined together only in the 4 or 5 positions as α - or β -glucosides.

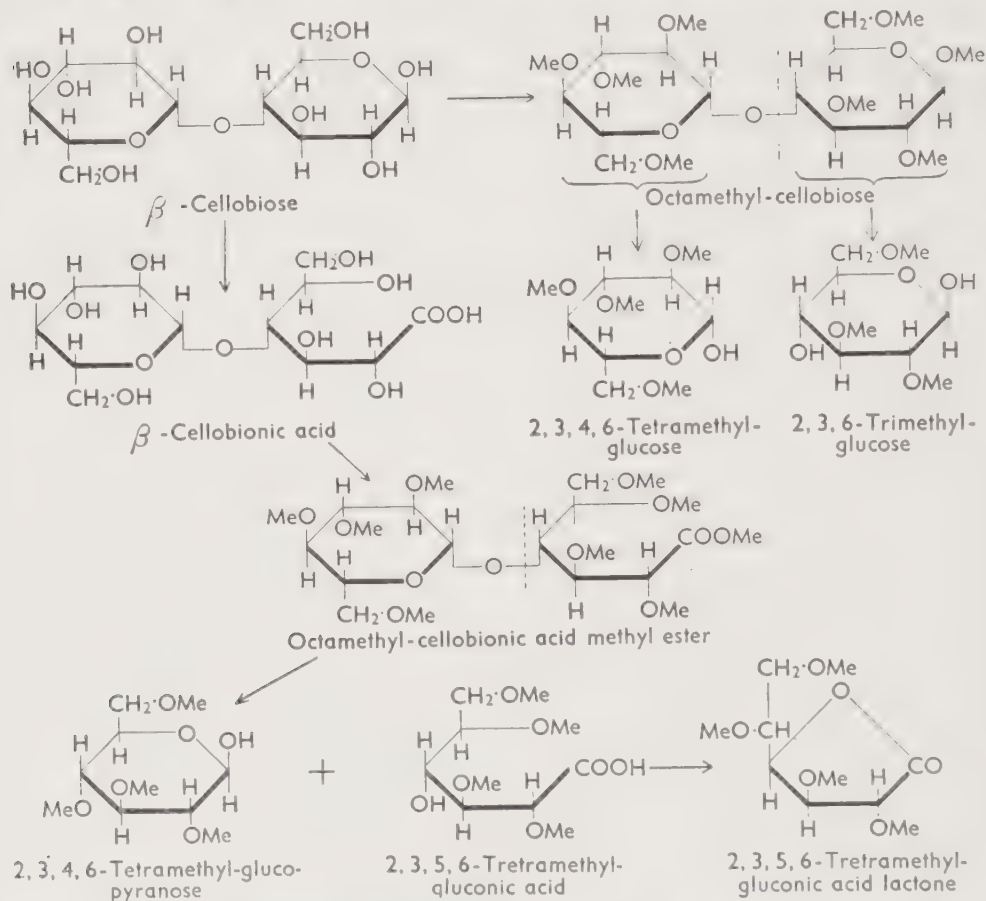
In this phase of the development the finding of Haworth (42), that sugars normally occur in the form of pyranose rings, became of great importance. It made it highly probable, that the glucose units in the cellulose were linked up by 1,4 bridges and not by 1,5 bridges.

The 1,4 linking was finally substantiated by the determination of the constitution of cellobiose by Haworth and co-workers (43). When cellobiose was treated with dimethyl sulfate and NaOH, an octamethyl derivate was obtained, which when hydrolyzed yielded equimolar amounts of 2,3,6-trimethyl- and 2,3,4,6-tetramethylglucose. Furthermore, cellobiose was oxidized to cellobionic acid, which was methylated to octamethylcellobionic acid methyl ester. This, upon hydrolysis, gave 2,3,4,6-tetramethylglucose and the γ -lactone of 2,3,5,6-tetramethylgluconic acid. The results of these two degradation reactions showed, that the non-reducing half of cellobiose was linked up by means of a glucosidic oxygen bridge with the hydroxyl group in position 4 of the reducing half. The constitution of cellobiose had therefore been shown to be that of a 4-D-glucopyranosyl-D-glucopyranose. This proof of the structure of cellobiose is illustrated in the diagram on the following page.

In the acetolytic breakdown of cotton cellulose, besides the octaacetylcellobiose acetylated oligosaccharides containing more than two glucose residues are also formed. A cellotriose was isolated first by G. Bertrand and S. Benoist (44) and later by Irvine and Robertson (45) and by H. Ost (46), and a cellotetraose by Freudenberg and co-workers (47). R. Willstätter and L. Zechmeister (48) found that both cellotriose and cellotetraose also were formed in hydrolysis of cellulose by means

of fuming hydrochloric acid. The concept that cellulose consists of a chain of glucose residues, thus received strong experimental support.

The relationship between the oligosaccharides mentioned above and the cellobiose was revealed by L. Zechmeister and G. Toth (49) and by K. Freudenberg and his co-workers (50). The former workers found that the acetolysis of cellotriose yields octaacetylcellobiose, so that cellotriose may be regarded as a cellobiosido-glucose. Freudenberg prepared



completely methylated cellobiose, cellotriose, and cellotetraose, and succeeded in preparing the first two synthetically, by the action of trimethyl-methylglucoside on the chlorohydrins of methylated glucose or cellobiose. W. N. Haworth (51), by step-wise hydrolysis of trimethyl-cellulose, followed by further methylation, also succeeded in preparing octamethylcellobiose and hendecamethylcellotriose in crystalline form. The latter compound was identical with Freudenberg's preparation.

By using a chromatographic technique, E. E. Dickey and M. L. Wolfrom (51 a) recently were able to isolate from an acetolysis mixture the α -D-acetates of glucose, cellobiose, -triose, -tetraose, -pentaose, and

-hexaose in a crystalline state. As the number of glucose residues increases, the melting points and the specific rotations of these products approach the corresponding values for cellulose triacetate.

On the basis of the optical rotation of the methylated degradation products of cellulose K. Freudenberg (27, 52), using the rule of optical superposition, had also concluded that only β -glucosidic linkages were present. His belief was strengthened by studies of reaction kinetics. "Even one α -linkage to 100 β -linkages would be detectable," he remarked (53). Staudinger (54) has remarked that a considerable extrapolation is necessary to arrive at the conclusion that only β -linkages are present in the cellulose molecule, since only the smallest fragments of the cellulose breakdown can be studied.

In several organisms, as in thermophilic cellulose bacteria (55), in the hepato-pancreatic juice of the edible snail, *Helix pomatia* (56), and in molds (57), enzymes occur, which are able to hydrolyze cellulose. It could be shown (58, 57), that two enzymes cooperate. The first of them, cellulase, breaks down cellulose to oligosaccharides with an average length of 6 glucose residues, and the second one, cellobiase, hydrolyzes the oligosaccharides and cellobiose to glucose. As cellobiase has to be classified as a β -glucosidase (59, 57), its action confirms the existence of β -glucosidic linkages in the cellulose.

The question of the number of glucose or cellobiose residues in the cellulose molecule has been considered since a fairly early date, as has been pointed out above (25). Various estimates have been made from *determinations of the end groups*. M. Bergmann and H. Machemer (60) have proposed that the end group be determined with sodium hypoiodite by the method of Willstätter and Schudel, on the assumption that it is an aldehyde group. The average degrees of polymerization calculated from the hypoiodite consumption actually agree with those obtained from osmotic pressure and viscosity measurements in the case of *degraded* cellulose, as H. Staudinger and K. Eder have shown (61). It is doubtful, however, if this method can be used for native cellulose, or for that which has been only slightly degraded (62). The copper number cannot be used for this determination.

E. Schmidt (63) assumes that the terminal aldehyde group is oxidized to carboxyl. The carboxyl was determined in various ways, and Schmidt assumed on the basis of these results that the chain consists of about 100 glucose residues (64).

Other investigators (65) have expressed the opinion that cotton cellulose has a COOH group (instead of a primary alcohol group) after every 500 glucose molecules, and that wood cellulose has one after every 96-100

residues. This would constitute a fault or weak point, offering lessened resistance to chemical and mechanical influences.

E. Husemann and O. H. Weber (65, 66) supposed that native fiber celluloses are monocarboxylic acids. The carboxyl groups were quantitatively determined by the "reversible methylene-blue" method of O. H. Weber. The wood celluloses on the other hand were believed to be polycarboxylic acids, in which a macromolecule contains 9-12 carboxyl groups.

E. Heymann and G. Rabinov (67) also assume the presence of acid groups in cellulose. When cellulose is treated with a neutral salt solution, a certain amount of acid is liberated. The acidity of this acid is determined not by the OH groups but probably by carboxyl groups. Oxidation of the cellulose increases its acidity. The "soluble cellulose acid" was titrated potentiometrically with baryta, and found to be somewhat stronger than acetic acid. (Calculation of the partition of a base between two acids in this case, or of the Donnan equilibrium, proved unreliable.)

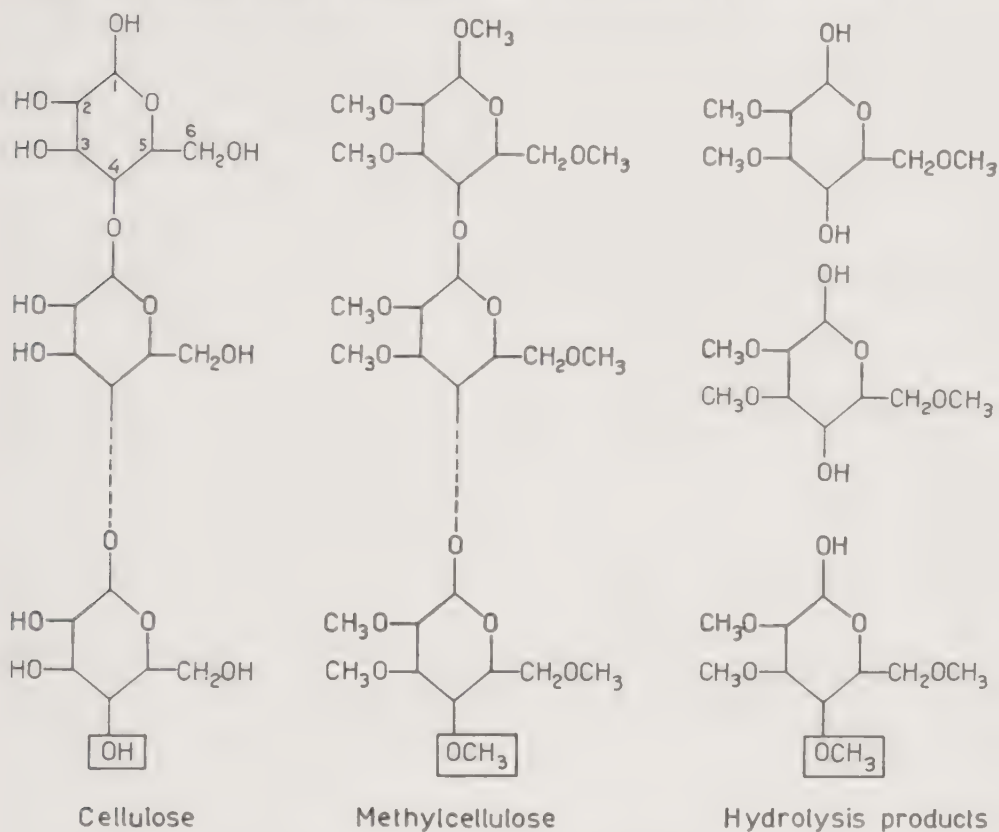
Recently, A. J. A. van der Wyk and M. Studer (67 a) have published a critical discussion of the methods hitherto used in the determination of the acidity of cellulose. Basing their considerations on the theory of Donnan, they state that it is possible to titrate insoluble acids like cellulose only if an excess of a strong electrolyte is present during the titration. On titration of different celluloses suspended in 0.6 *N* sodium chloride solution, they found the following dissociation constants:

	K
Native cotton.....	$8 \cdot 10^{-8}$
Cotton, reprecipitated from cuprammonium solution.....	$5 \cdot 10^{-8}$
Sulfite pulp (containing 98 % α -cellulose)...	$4 \cdot 10^{-7}$

α -Hydroxy acids like α -D-galacturonic acid, glycolic, and lactic acid have dissociation constants of the order of magnitude of 10^{-4} . Thus, cellulose is 10^3 to 10^4 times weaker than the hydroxy acids. From this result the authors conclude that the pure celluloses do not contain any carboxyl groups, but that the acid character of cellulose is due to the accumulation of hydroxyl groups.

K. Freudenberg and E. Braun (68) attempted in 1927 to employ a different method for determining the end groups of the cellulose chain, and hence its molecular size. If one accepts the formula for cellulose given in the scheme below it is obvious that complete methylation and subsequent acid hydrolysis, as first performed by Irvine and Hirst (41), must give two different methylated glucoses; one of the two end groups must yield

2,3,4,6-tetramethylglucose, while the other glucose residues yield 2,3,6-trimethylglucose. This is illustrated by the following scheme (68 a):



Freudenberg and Braun, however, after hydrolyzing 30 g. of trimethylcellulose, were able to isolate only 2,3,6-trimethylglucose and no tetramethylglucose. From this they concluded that the cellulose chain is perhaps many hundreds of glucose units long. Haworth and Machemer (69) later obtained 0.5 % of tetramethylglucose, corresponding to a chain length of 100-200 glucose residues. Several years later Haworth and his co-workers (70) found that 1 mol. of tetramethylglucose was formed for every 700 glucose residues. Freudenberg and Plankenhorn (71, 72, 73, 74) then methylated unbleached ramie fibers under mild conditions, and obtained a value for tetramethylglucose corresponding to a chain length of 2,000 glucose residues, and finally Hess and his co-workers (75, 76) who improved the method for determining tetramethylglucose, found that very little if any tetramethylglucose can be obtained from native cellulose (cotton fibers prepared under particularly mild conditions).

These results show unmistakably that the molecular weight of native cellulose must be very great, and that those results of end-group deter-

minations which indicate shorter chains are due to partial degradation of the original macro-molecule, caused, for example, by methylation under too strenuous conditions.

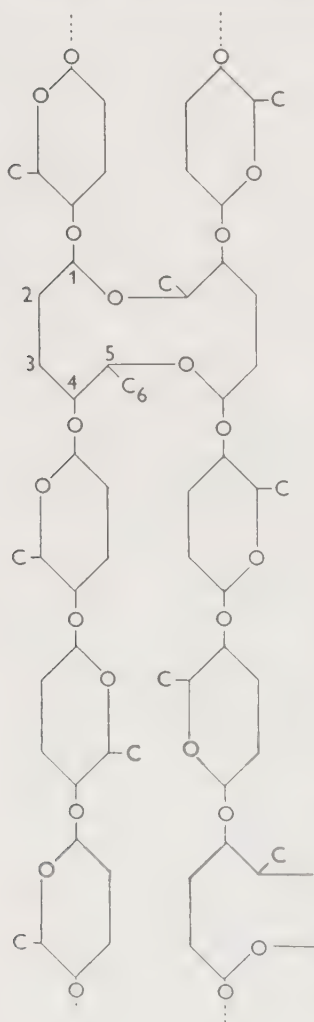
There is no simple connection between the end-group values (EG) and the viscosities of different cellulose preparations (77).

It turned out that cellulose preparations with the same viscosity showed considerable differences in EG, depending on whether the cellulose had been prepared by hydrolytic, oxidative, or photochemical degradation. Hess explained this by assuming that two different kinds of linkages are present in cellulose. One of them can be broken without changing the EG, while splitting the other entails a change in the EG. This would be true if, besides the glucosidic linkages *along* the chains, there were isolated oxygen bridges connecting the chains in a network. The possibility of such a network-formation had already been considered by K. H. Meyer

and H. Mark (78) in connection with a discussion of the micellar structure. This question has been discussed in more detail, for the case of proteins, by A. Frey-Wyssling (79). If networks really are formed, it may be impossible to determine the average length of the cellulose chains by measurement of the EG.

From the fact that it was not possible to introduce the theoretical number of alkyl groups into cellulose on alkylation, P. Karrer and E. Escher (80) concluded that cross-linkages exist between adjacent hydroxyl groups of neighboring cellulose chains.

K. Hess and E. Steurer (77) found that methylcellulose dissolved in dioxane decreases in viscosity when it is illuminated with ultraviolet light, but that a corresponding increase in the end groups could not be observed. The explanation might be that cross-linkages are present which are more easily split by the ultraviolet light than are the glucoside linkages in the chain. These authors think that such cross-linkages might arise by the opening of the 1,5 oxygen ring in occasional glucose molecules. If this occurred in adjacent glucose molecules, a linkage of the carbon atom 1 in one glucose to the carbon atom 5 in the residue of the other chain might occur (see Fig.).



Similar observations, made by Freudenberg and co-workers (71, 74), were explained by these authors in a different way. They found that methylcellulose, with a methoxyl content of 43-44 %, which had been prepared from ramie fiber with dimethyl sulfate in cold alkali, gave highly viscous solutions in chloroform, while another methyl cellulose, which had been obtained with sodium and methyl iodide in liquid ammonia, and contained 42 % OCH_3 , gave solutions of low viscosity. The viscosity of the high-viscous methyl cellulose decreased upon treatment with sodium in liquid ammonia at minus 70°C . A very small increase in the end groups, which could not account for the decrease in viscosity, was observed. The authors concluded that sodium, in the presence of ammonia effects a separation of chains, which in the original fiber were held together by associative forces.

It has been abundantly established that it is possible to form cross-links between neighboring chains by various chemical procedures [cf. the reviews by E. Heuser (81) and by W. G. Cameron and T. H. Morton (81 a)]. One of them is the formaldehyde treatment of rayon silk fibers, probably resulting in the formation of methylene bridges between hydroxyl groups of adjacent chains. A 1-2 % methylene content suffices to cause extensive changes in the characteristics of the fiber (82). These changes consist chiefly in diminished swelling in water, decreased solubility in alkali and in ammoniacal copper oxide, and a considerable increase in the wet tensile strength which is unfortunately accompanied by a decrease in the extensibility.

Another procedure for the introduction of cross-linkages consists in esterification with dibasic acids. Only one carboxyl group is esterified. The cellulose phthalate of C. J. Malm and C. R. Fordyce (83) may be quoted as an example. The barium salt of this compound is evidently cross-linked, since it unites two cellulose chains. This salt proved to be insoluble in water, although the sodium salt was easily soluble.

The same considerations apply to certain oxycellulose compounds, which contain relatively large numbers of carboxyl groups. Examples of such compounds are those formed by nitrogen dioxide (84). Calcium salts of these compounds are insoluble in water, but the salts with monovalent cations are soluble.

We shall return to the question of the length of the cellulose chains later, in connection with the discussion of the molecular weight.

The results concerning the structure of cellulose, obtained during the twenties chiefly by purely chemical means (cf. pages 42-44), were at the same time strongly supported by *X-ray examination*, especially when it became possible to interpret the X-ray measurements correctly.

C. v. Nägeli observed (85) over half a century ago that plant membranes, like cell walls and fibers, are optically anisotropic. He conceived that these membranes were built up of submicroscopic, anisotropic bodies which he called *micelles*. His idea was generally disregarded during the succeeding period, but received support from H. Ambronn's studies on the anisotropy of cellulose (86). Nägeli's theory was proved only when P. Scherrer, using the X-ray technique for determination of molecular structure (M. v. Laue, 1912) succeeded in showing a clear crystalline structure in a ramie-fiber preparation of Ambronn (87).¹ At about the same time, R. O. Herzog and W. Jancke (89) published some studies on the crystalline structure of cellulose in various materials, including wood. They always obtained the same X-ray diagram, and hence concluded that cellulose was always the same chemical substance, no matter what its source.

Refinements of the X-ray technique by M. Polanyi, K. Weissenberg, and others (90) led the former to undertake the measurement of the "unit cell" of cellulose. The unit cell is the smallest unit of the crystal lattice from which the entire crystal can be built up by displacements parallel to the axes. These investigations were continued by other workers, using the most varied cellulose preparations (91). The conclusion was drawn that the dimensions of the cell were such that only a small number of glucose-anhydride residues could be contained in it. This led to the erroneous idea that the cellulose molecule consisted of small units such as tetraoses, which were held together by secondary valences (92). Hess (93) concluded from a study of the optical rotation of cellulose in cuprammonium solution that the cellulose consisted of glucose-anhydride residues which were held together by association in the solid cellulose, but dissociated on solution. This notion has been disproved by various workers (94).

The study of the constitution of organic substances by X-ray investigations was meanwhile greatly advanced by W. H. Bragg and his school (95). On the basis of the atomic radii of carbon and oxygen determined by these investigations, O. L. Sponsler and W. H. Dore (96) calculated the diameter of the hexose molecule of Haworth and found it to be 5.13 \AA ($0.513 \text{ m}\mu$). The interference pattern also corresponded to the Haworth pyranose formula. Investigation of the X-ray diagram of a cellulose fiber also revealed a periodic structure, repeating itself every 10.25 \AA in the direction of the fiber. This figure, which is nothing more than the length of the unit cell along the fiber axis, corresponds exactly to the length of

¹ E. Heuser (88) has pointed out that the Japanese workers Nashikawa and Ono had made X-ray studies of textile fibers as early as 1913, and had concluded from them that the fibers were composed of minute crystals oriented parallel to the axis of the fibers.

two glucose units (cf. Fig. 34) (97). This discovery agreed perfectly with the idea arrived at by chemical means that cellulose is built up of cellobiose units. [Sponsler wrongly assumed that the glucose residues were held

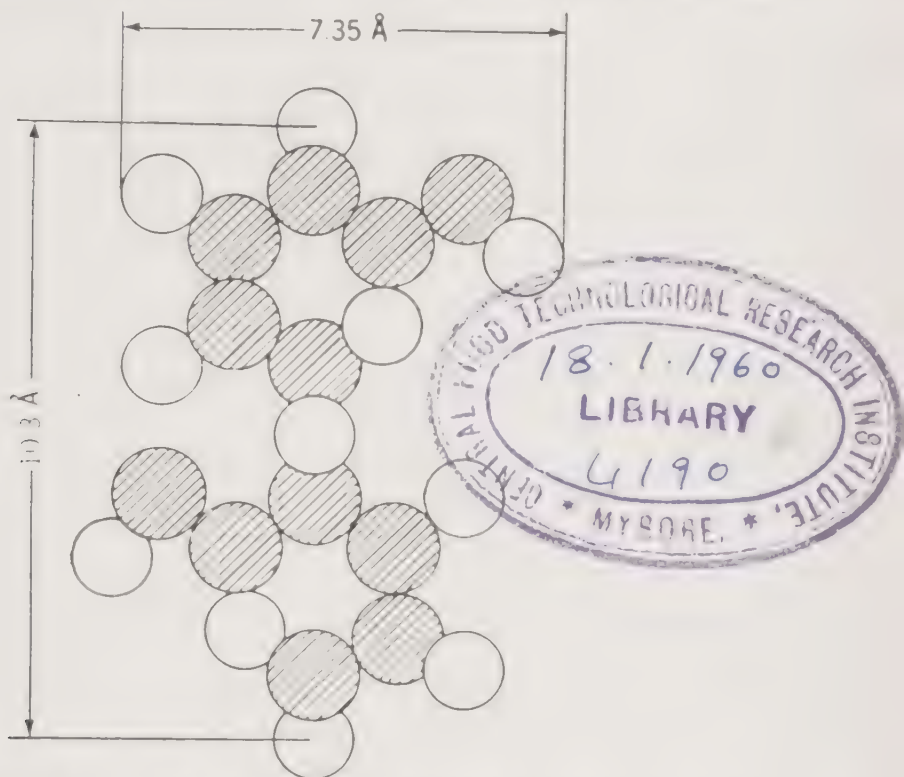


Fig. 34. The cellobiose molecule. The shaded circles represent carbon atoms, and the smaller circles, oxygen atoms.

together by alternate 1,1 and 4,4 linkages, instead of by the 1,4 linkages which are characteristic of cellobiose. W. N. Haworth was the first to correct this error (98)].

The question as to why a structure corresponding to two glucose residues repeats itself periodically in the direction of the fiber axis was cleared up by K. H. Meyer and H. Mark (99), who showed that such a period can be explained on the assumption of a digonal screwing. The two glucose groups in a cellobiose unit of the cellulose are turned at an angle of 180° .

In Fig. 35 the arrangement of the chains in the *elementary cell of native cellulose*, as given by K. H. Meyer and L. Misch (100), is shown. It will be noted that all of the chains do not run in the same direction; on the contrary, two groups of chains running in opposite directions are involved in making up the crystal.

Different kinds of forces are operative in this crystal. The cellulose chains, running along the *b*-axis, are built up by strong covalent bonds.

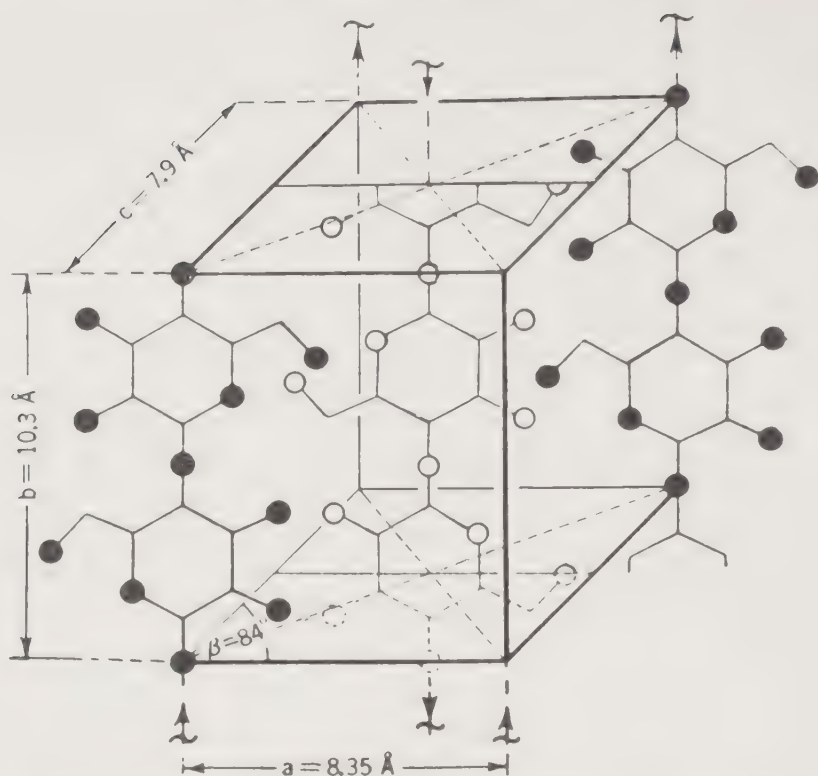


Fig. 35. Schematic representation of the unit cell of native cellulose (after Meyer and Misch).

They are, however, also held together with their neighbors by secondary forces. Thus, hydrogen bonds are established between adjacent glucose residues situated in the ab -planes. Fig. 36, 37, 38 are projections of the unit cell perpendicular to the b -, a - and c -axis (100). The carbon and oxygen

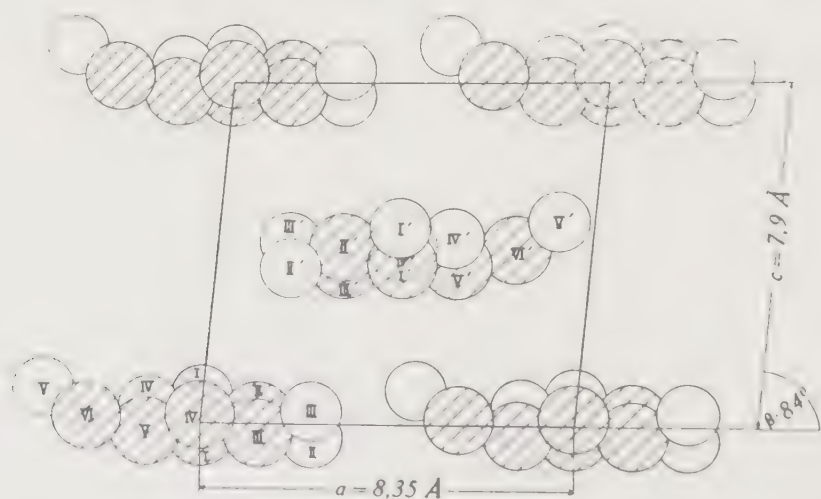


Fig. 36. Projection of the elementary cell of cellulose on the plane ac .

atoms are given by their covalent radii, the hydrogen atoms have been omitted as in the foregoing Fig. 35. Mark (101) has pointed out that the distances between the OH groups in the ab -planes fall within the range which according to L. Pauling (102) and M. L. Huggins (103) makes the

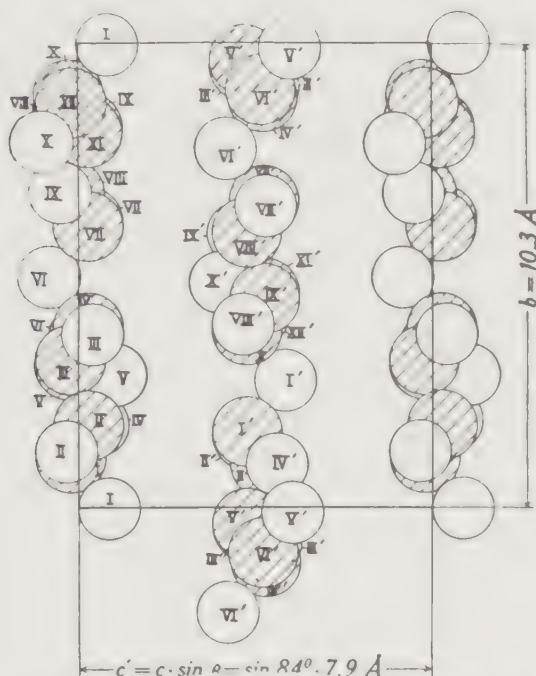


Fig. 37. Projection of the elementary cell of cellulose on the plane bc .

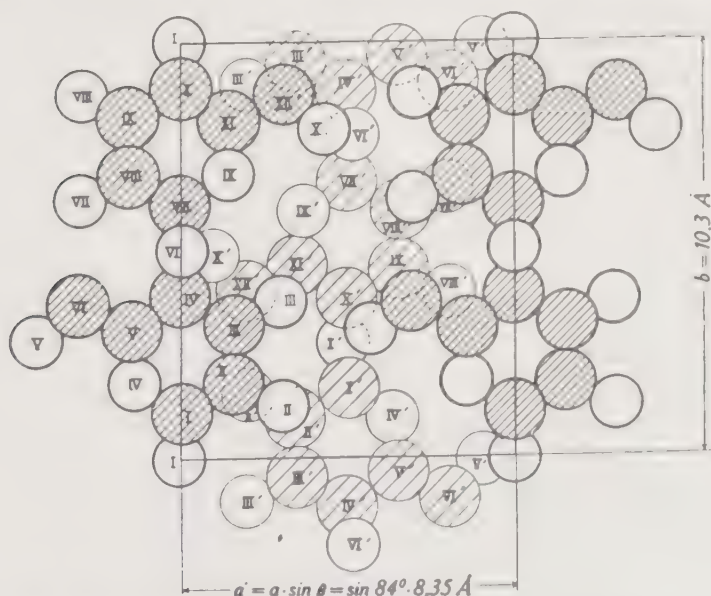


Fig. 38. Projection of the elementary cell of cellulose on the plane ab .

formation of hydrogen bridges probable. Their existence has been supported by infrared absorption measurements (104). In the *bc*-planes only weak polar forces between the cellulose chains can exist.

P. H. Hermans (105) has investigated the spatial arrangement of the macromolecules inside the micelle. On the basis of the now well-known valence angles, interatomic distances and atomic radii, he constructed and discussed a stereochemical model of a cellulose chain, consisting of glucopyranose residues linked together as 1,4- β -glucosides. He also discussed the packing of straight chains, lying parallel to one another. It turned out that if the cellulose residues were to fit into the 10.3 Å period which has been determined by X-ray spectrography, an angular position of the chain was required, and the glucose groups could not lie exactly parallel to one another. The bending of the chain was both horizontal and vertical. This model differed only slightly from that derived by K. H. Meyer and L. Misch (100) on the basis of the X-ray data. A study of these models also showed that the packing of the parallel chains could be brought into harmony with the X-ray data if the successive chains in the direction of the *c*-axis had alternating polarities, and were displaced relative to one another in the direction of the fiber axis; this was also the case in the model of K. H. Meyer.

The β -glucosidic structure of cellulose probably means that the glucopyranose rings occur in the chair form, for this form can be joined together in the 1,4 positions to make straight chains. [In starch, on the other hand, which is known to be α -glucosidic, the pyranose rings occur in the boat form (106)]. Hermans (105) has called attention to the fact that the β -glucosidic structure in the chair form has all the hydroxyl groups on the two edges of the plane of the cellulose chain which is formed by the somewhat bent pyranose rings, while only hydrogens project before and behind the plane. The cellulose chain is therefore hydrophilic in two directions and hydrophobic in the other two; it is possibly this circumstance which makes cellulose so much less soluble in water than is starch, which has its hydroxyl groups distributed in all directions.

In a recent paper, A. J. A. van der Wyk and K. H. Meyer (107) come to the conclusion that the structure model proposed by Meyer and Misch (100) is still the best approximation available, and that the introduction of stereochemical data [Hermans (105)] probably could not give further detailed information.

It has already been stated that cellulose molecules in native fibers have been found to run parallel to one another, and to be arranged in a lattice. This lattice is, however, not continuous in all parts of the fiber, but is interrupted both in the lengthwise and crosswise directions. The ordered

regions are identical with the micelles of Nägeli. H. Mark and K. H. Meyer attempted to calculate the *dimensions of the micelles* from the breadth of the X-ray interference patterns, and other investigators have also studied this question (108). The length in the direction of the fibers varies between 600 and 1,500 Å for cotton and ramie; the dimension, perpendicular to the fiber axis was 60-80 Å.

A. N. J. Heyn (109) has studied the small-angle scattering of X-rays and found that different fibers gave completely different scattering patterns. This was assumed to be due to differences in the size of the micelles and the intermicellar distances. According to this investigation, it seems probable that hemp, flax, and jute have smaller micelles than ramie and cotton.

X-ray studies by S. Berkman, J. Böhm, and H. Zocher (110) showed that intermicellar spaces were present. These authors precipitated colloidal gold and silver in the fibers by means of the process of H. Ambronn (111). The fibers so treated gave unchanged X-ray diagrams, but with the diagrams of the crystalline metals superposed. This indicated that the metallic precipitates filled the intermicellar spaces. A. Frey-Wyssling (112) calculated the diameters of the intermicellar spaces from the distances of the interference figures in the metal diagram and found values between 50 and 100 Å, i.e., in certain cases, twice as great as the ordered regions. O. Kratky and F. Schossberger (113) showed by the same method that the width of the micelles in a ramie fiber was 50-60 Å. The intermicellar spaces obviously cause the differences in density of plant fibers.

Attempts have been made to determine the total internal surface of fibers by measuring the adsorption capacity for gases, as for instance, nitrogen at minus 195° C. In the case of cotton a value of 0.72 m² per gram has been found by this method (114).

The model of a cellulose fiber first proposed by Meyer and Mark (115) in which the ordered-lattice regions or micelles are closed entities, laid parallel to one another like the bricks in a wall, is no longer acceptable (116).

According to A. Frey-Wyssling, the intermicellar spaces which run longitudinally communicate with one another and form a submicroscopic capillary system in the fiber (cf. Fig. 39).

In Fig. 39 the black portions represent the spaces and the white portions the regions filled with cellulose chains. Regular, closed micelles are not to be seen here. Of course, the fibers are built up of parallel cellulose chains in this case, too. They are, however, not all of the same length. The chains run through ordered regions, which are outlined in the figure with dotted lines. A single chain can, then, belong to many micelles (117).

Between the micelles, the position of the cellulose chains may be irregular; thus amorphous regions arise. The ends of the chains do not necessarily lie in these regions; the chains can also end in the crystalline regions, but

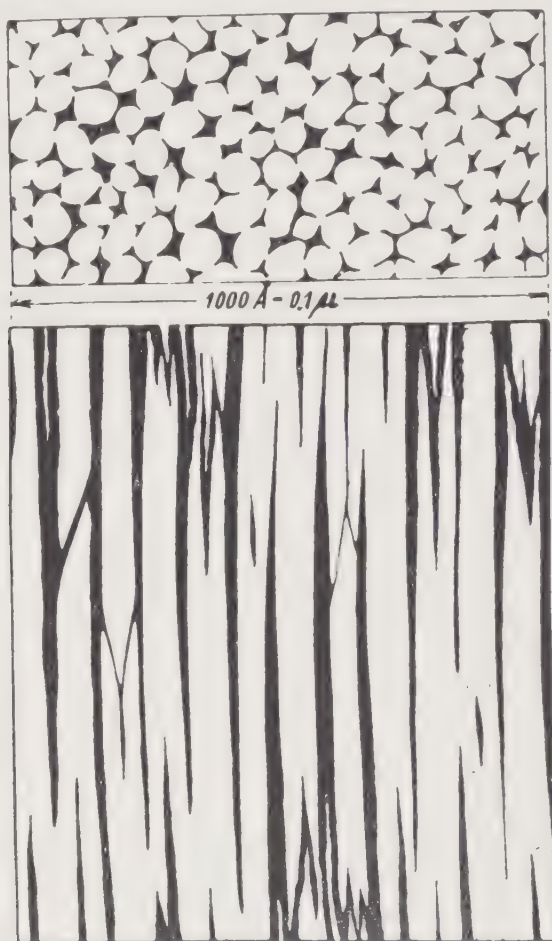


Fig. 39. The structure of bast fiber, according to Frey-Wyssling. Above, transverse section; below, longitudinal section.

The intermicellar spaces are shown in black; the white portions of the figure represent the spaces occupied by cellulose chains.

be distributed at random there—"macromolecular lattice" of Staudinger (118) (Fig. 40).

The assumption of cellulose chains which run through two or more crystalline regions explains the extremely high tensile strength of native cellulose fibers as compared to other materials (119). The strength sometimes attains values not far below the theoretical values for the strength of the primary valence (covalent) bonds in the chain. The extremely great strength of swelled fibers, which may exceed that of the dry fibers, is evidence that the crystalline regions are bound together by primary

valence bonds, according to W. Schramek (120). The wet strength of artificial fibers is lower, evidently because there the crystalline regions are not bound together by primary valence forces.

The micelles from which individual chains project out, forming amorphous regions, as has been described above, have been termed "fringe micelles" by O. Gerngross, K. Hermann, and A. Abitz (121); the primary valences of the chains which extend through the fiber are considered to be responsible for the strength and for the extensibility of the fiber (122).

This picture is in agreement with the concepts of H. Staudinger, who thinks of native cellulose as being composed of cellulose molecules whose length is several times as great as the length of the micelle as determined by X-ray measurements.

It may also be mentioned that *electron microscopy* has been applied to the problem of fiber structure. For information about this subject the reader is referred to an article by G. R. Sears (123). Beyond the literature mentioned there some recent work may be quoted. K. Wuhrmann, A. Heuberger and K. Mühlethaler (124) treated cellulose fibers from ramie, hemp, cotton, etc., with ultrasonic waves for 3-10 minutes, obtaining very long and fine filamentary *fibrils*, most of which proved on electron-microscopic investigation to have a width of 60-70 Å. These fibrils obviously represent bundles of relatively few micelles. Artificial fibers treated in the same way behaved entirely differently. They showed no separation into long filaments. The separation of cotton cellulose by ultrasonic wave treatment into thin (50-100 Å wide) filaments (fibrils, rows of micelles) has recently also been demonstrated by B. G. Rånby and E. Ribi (124 a), cf. Figure 41. Electron micrographs of various celluloses after wet-beating in a Waring Blendor have been published by C. W. Hock (124 b). The fibers are broken down longitudinally into fibrils with an average width of a few hundred Ångströms.

P. H. Hermans (125) states that grinding of very dry cellulose fibers in an oscillating beater generally does not result in a

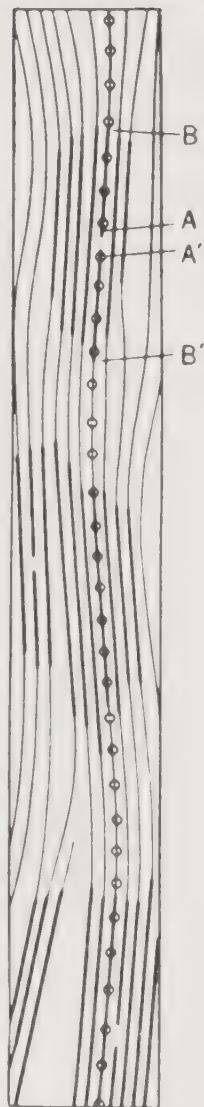


Fig. 40. Cellulose micelles, held together by «primary valence chains» (cellulose molecules) (after Kratky and Frey-Wyssling).

The two molecules B and B', marked with circles, behave like a single molecule running through the whole structure because the ends A and A' lie inside a crystalline region (micelle).

distinct splitting up into "elementary fibrils," as it had been claimed by K. Hess and co-workers (126) and by W. Wergin (127).

Cellulose films produced by *Bacterium xylinum* or *Bacterium xylinoides* have been examined in the electron microscope by several authors



Fig. 41. Electron micrograph of cotton cellulose treated with ultrasonic waves. Shadowed with palladium and gold.

(128, 129). The existence of crystalline cellulose threads of about equal diameter (200 Å) embedded in a diffuse film of cellulose has been revealed by these studies.

In this connection it is necessary to discuss the very important question of the chemical reactivity of cellulose *in the solid phase*. As has already been pointed out, it has been shown in various ways that native cellulose consists of crystalline and amorphous regions. It is also quite certain that the accessibility of various parts of the fiber to chemical reagents depends very much upon the degree of crystallinity, since the crystalline regions are penetrated by the reagents only with difficulty. These circumstances are naturally very important for the preparation of cellulose derivatives.

Various attempts have therefore been made to determine the relative volumes of the easily accessible, *amorphous regions* and the difficultly accessible, *crystalline regions* of the cellulose fibers.

It was at first impossible to obtain exact quantitative data from X-ray spectrography, but under certain conditions O. Kratky and A. Sekora (130) succeeded, by using the X-ray diffraction at small angles, in determining the quantity of crystallites in fibers, and Flaschner and Kast (131) have recently reported that they were able to make a quantitative estimate of the diffuse scattering caused by amorphous material. The crystalline portion of a fiber of cuprammonium rayon was calculated from the X-ray diagram as 4-10 %.

An extensive investigation of the intensity of scattered radiation in native and regenerated cellulose materials has been carried out by P. H. Hermans and A. Weidinger (131 a). After certain corrections, the intensity of the diffuse background could be assumed to be a correct relative measure of the amorphous portion. Thus, within a series of native fibers, such as cotton, cotton linters, ramie, and flax fibers the amount of the crystalline portion was found to be equal, viz., $70 \pm 2\%$. In wood pulp, the ordered fraction was slightly lower and in bacterial celluloses considerably lower. Also within a series of regenerated celluloses, including viscose rayons, cellophane, Lilienfeld rayon, and cuprammonium rayon, the crystalline portions were equal, viz., $39 \pm 3\%$.

On the basis of density determinations P. H. Hermans and his co-workers (132) report that native cotton and ramie fibers are about 60 % crystalline, and that viscose fibers contain only about half as much crystalline material.

P. H. Hermans, I. I. Hermans, and D. Vermaas (133) determined the density of natural and artificial cellulose fibers by observing the temperature at which the fibers just remain suspended in carbon tetrachloride, without either sinking or floating; this temperature ranged between 45 and 65° C. The following values were obtained:

	Density at 20° C.
Ramie.....	1.554
Ramie, mercerized.....	1.545
Cotton, bleached.....	1.545
Wood cellulose, α -fiber.....	1.537
Bemberg silk.....	1.524
Viscose, unstretched.....	1.518
Viscose, stretched 120 %.....	1.523

If it is assumed that the density of the amorphous region is 5-6 % less than that of the crystalline portion of the fiber, it may be calculated that the native ramie fiber is 55-60 % crystalline, and the viscose, 20-25 %.

According to P. H. Hermans (133 a), the quantity of amorphous material in cellulose fibers should be nearly proportional to their sorptive capacity for water vapor. On this basis, the amount of crystalline fraction was estimated to be 68 % in native and 35 % in regenerated celluloses.

From the foregoing it can be seen that the figures calculated by P. H. Hermans on the basis of different physical data are in reasonable agreement.

In this connection the investigations of various authors (134) on the exchange of the hydroxyl hydrogen of cellulose with deuterium are of interest. It was found that all of the hydroxyl groups of the cellulose eventually reacted; the exchange proceeded very rapidly at first, but dropped off sharply after a short time (135). One of the possible interpretations of this fact is that the hydroxyl groups in the amorphous region are more readily exchanged than those in the crystalline region. In a rayon pulp, 34 % of the hydroxyl groups were readily exchangeable.

The studies of C. A. Harris and C. B. Purves (136) and of A. G. Assaf, R. H. Haas, and C. B. Purves (137) also illustrate the varying accessibilities of the different hydroxyl groups. These authors come to the conclusion that only the hydroxyl groups which lie on the surface react with thallium ethylate in diethyl ether or benzene, because the thallium atoms are too large to penetrate the crystalline regions. The number of accessible hydroxyl groups is determined by treating the thallium alcoholate compound of cellulose with methyl iodide, and determining the extent of methylation. By this method a very small value, 0.4 %, was obtained for the amorphous fraction of cotton linters. On the other hand, 27 % amorphous region was found in linters which had been swelled with sodium hydroxide solution.

G. Goldfinger, H. Mark, and S. Siggia (138) oxidized linters and cellulose regenerated from Schweizer's solution with sodium periodate, and found evidence that the amorphous region is easily attacked, while the crystalline region is only slowly oxidized. After a rapid initial phase, the rate of oxygen consumption decreased and continued linearly at the lower rate. An attempt was made to obtain an approximate measure of the easily-accessible portion of the fiber by extrapolating the linear part of the curve back to zero time.

T. Timell (138a) has followed the reaction of various ammonia celluloses with sodium in liquid ammonia by determining the amounts of hydrogen evolved. This reaction was also found to be initially rapid and later much slower. The conversion-time curves showed that cotton linters contained approximately 40 % of accessible material, sulfite pulp 45 %, and viscose rayon 60 %. These values are in reasonable agreement with

those obtained by physical methods (see above). The same author has also given a very valuable review of the other methods used hitherto for estimating the amounts of amorphous (accessible) and crystalline material in various celluloses.

Another chemical method for determining the accessibility was presented by L. Jorgensen (138 b). It is based upon the reaction of the cellulose fibers with chromium trioxide in acetic acid-acetic anhydride mixture. This method, too, showed that cotton linters are less accessible than sulfite pulps.

R. F. Nickerson (139) has employed an hydrolytic-oxidative method for the quantitative determination of the non-crystalline region. The cellulose is boiled with a solution 2.5 *N* in HCl and 0.6 *M* in FeCl₃, and the progress of the hydrolysis is followed by the amount of carbon dioxide evolved from the split products (particularly glucose). The rate of hydrolysis is rapid for the first few minutes, and then decreases gradually, becoming nearly constant after one hour. Nickerson concluded from this procedure that cotton contains 3 % of amorphous (easily hydrolyzable) and 94 % of crystalline (difficultly hydrolyzable) material, while the remaining 3 % consists of "mesomorphous" transition stages. Hydrolysis with 2.5 *N* sulfuric acid and volumetric determination of the glucose formed leads Nickerson and Habrle (140) to similar results.

The rate of hydrolysis in 4 *N* HCl at 100° C., as measured by the weight of the residue, has also been employed to determine the amorphous and crystalline fractions of fibers (141).

The following figures may be quoted:

Fiber	Crystalline Cellulose, %
Ramie	95
Cotton	82-88
Mercerized cotton	68-78
Staple fiber	68
Fortisan silk	83
Cord silk	62

F. C. Brenner, V. Frilette, and H. Mark (142) have recently questioned the value of such hydrolytic methods. They found that a formation of new, crystalline cellulose proceeds hand in hand with the hydrolytic degradation of the amorphous cellulose. The increase in density of the residual material was greater than could be accounted for by the observed loss in weight (due to the decomposition of the amorphous material). For example, when a beech wood cellulose had lost 6 % of its weight, it could be calculated that the crystalline material had increased by 18 % [assuming the density of amorphous cellulose to be 1.50, (143), and that of crystalline cellulose, 1.59 (144)], while a rayon showed a 16 % increase in

crystalline material when 10% of the weight had been lost. On the basis of moisture regain studies, J. A. Howsmon (141 a) also came to the conclusion that a recrystallization must have taken place during the first stages of hydrolysis.

Similar effects have been observed by Hermans and Weidinger (144 b) who used their X-ray method (133 a) in order to determine the changes in crystallinity. They found that upon treatment of viscose rayon fibers with boiling 2.5 N sulfuric acid, the crystalline fraction is increased from 39 to 49 % within half an hour, and remains constant upon prolonged treatment.

It will be noted from the foregoing that the relative amounts of amorphous and crystalline cellulose as determined by different methods vary considerably. This is not surprising, since in the first place, the word "amorphous" does not describe any single well-defined state, but rather a range of states with varying densities of packing, and in the second place, the various reagents employed will have different effects even upon the same material.

Oddly enough, the grinding of dry cellulose fibers results in the destruction of the crystalline structure. However, the cellulose powder which results can be partially crystallized by the addition of hot water.

This extremely interesting observation has been reported first by K. Hess, H. Kiessig and J. Gundermann (145). On recrystallization of the amorphous product, hydrate cellulose was obtained. This finding was confirmed by P. H. Hermans and A. Weidinger (146), who stated that in the case of ramie fiber the recrystallized product contained 60-70 % of crystalline substance.

The complex structure of the cellulose fiber, with its various morphological parts (cf. p. 361) and its less accessible (crystalline, micellar) and easily accessible (amorphous) regions, is also reflected in the manner in which the *chemical reactions of the fiber* take place, e. g., ester and ether formation, and xanthation. A lively discussion between two opposing schools has been going on in this field for more than twenty years. It has recently been critically surveyed by T. Timell (138 a). One of these schools, represented by Hess, Lieser, Schramek, and others, is of the opinion that most of the cellulose reactions are of the *micellar-heterogeneous* type, i. e., they involve a rapid and complete conversion of the micellar surface after which the micelle itself reacts layer after layer, an inner core of unchanged cellulose remaining until the end. The other school, represented by Ambrom, Miles, Mathieu, Krüger, Staudinger, and several others, assumes that all the cellulose chains of a fiber have about the same probability of being converted, the reaction taking place in the

same way throughout the whole material, but more rapidly in the amorphous portions. This type of reaction is designated as the *permutoid* (or quasi-homogeneous) one.

T. Timell (138 a) found that in cases where swelling of the fibers and formation of addition compounds are effected before the conversion, the *permutoid* type of reaction is the most likely one. One example may be mentioned:

In 1939, H. M. Spurlin (147) outlined a method for determining the distribution of substituents in partially alkylated celluloses. This method has recently been used by T. Timell (138 a). It involves an estimation of the 2-, 3-, and 6-substituted glucose units, the number of glycol groups, and the amounts of unsubstituted, mono-, di-, and trisubstituted glucose residues. From these data, the relative amounts of the eight differently substituted glucose units can be calculated. By a comparison of the last-mentioned with the corresponding, statistically calculated values, certain conclusions can be drawn as to the course of the alkylation.

T. Timell has estimated the distribution of the substituents for some ethers prepared by treatment of cellulose, dissolved in quaternary ammonium bases, with alkyl halides. A comparison between the found and calculated values indicated that the entering groups were distributed according to the laws of probability.

The alkylation of native cellulose (cotton linters, sulfite pulp) with methyl sulfate and 35% alkali was also investigated. The estimation of the complete distribution of the methyl groups showed that the mono-substituted residues were mainly substituted in the 6-position, while the disubstituted residues were mainly the 2,3-derivatives. The amounts of unsubstituted and trisubstituted units present indicated, however, that no appreciable part of the fiber was inaccessible, and the alkylation reaction must accordingly be regarded as *permutoid* rather than *micellar-heterogeneous*.

Reactions which are carried out with unswollen fibers are often limited to the fiber surface. In other cases the molar volume of the reagent may be too great to allow penetration into the pores and interstices of the fibers. The above-mentioned reaction of cellulose with thallium ethylate (cf. p. 60) is an example of such "*surface reactions*". Finally, another type of reaction, designated as "*macroheterogeneous reaction*" [cf. Timell (138 a)] takes place if only certain parts of the fiber, i. e., either the primary or the secondary wall, are swelled and therefore easily penetrable.

The question of the *dissolution of cellulose* is of no less importance in the chemistry of cellulose.

The idea was quite wide-spread at the beginning of the nineteen-twenties

that cellulose and other polysaccharides were not high-molecular in the usual sense. On the contrary, it was believed that cellulose, for example, was composed of glucose- or cellobiose residues which were held together by secondary valences to form large aggregates, or micelles (148). Dissolved cellulose (in ammoniacal copper, for example) was supposed to exist in the form of glucose anhydride in sufficiently dilute solutions. The special properties of cellulose were attributed to a "skin" ("Fremdhaut") which enclosed the cellulose micelles (149). These views are no longer acceptable.

C. v. Nägeli's original idea that the cellulose micelles go into solution *as such*, should now be considered as refuted in the light of the actual micellar conception, micelles being not separate units but containing chains which may be common to several micelles (cf. p. 56).

Several authors, as T. Lieser (150), W. Schramek (151), O. Faust (152), and J. W. McBain and D. A. Scott (153), advanced the idea that the dispersed cellulose derivatives, e. g., xanthate, have the character of polymolecular particles. These particles have often been designated as "fringe micelles", as conceived primarily by O. Gerngross, K. Hermann, and W. Abitz (121). According to this view, dispersion occurs without disintegration of the molecular chains. Lieser found that only 0.5 xanthic ester groups per glucose unit are introduced into cellulose by ordinary xanthation. According to Schramek, it is possible by subsequent treatment of cellulose xanthate with carbon disulfide in alkaline solution to introduce further xanthic groups without affecting the crystalline parts. Schramek's interpretation is that only the fringes react completely, while the lattice-ordered part does not (151). He has supported this point of view by X-ray studies. H. L. Bredée (154), however, has criticized some of the experimental arguments given by Lieser and Schramek.

From other investigations, it seems to be evident that cellulose xanthate is molecularly dispersed in the viscose, at least in viscose solutions which have been diluted with alkali (155). A clear water solution, in which a molecular dispersion must be assumed, has been prepared by Lieser (156) by xanthation with carbon disulfide in tetraethylammoniumhydroxide solution and subsequent hydrolysis of the trixanthate obtained by dialysing its water solution. Such molecularly dispersed cellulose reacted with the calculated amount of copper hydroxide in the presence of ammonia.

Investigations carried out, among others, by G. Centola (157), G. Desmaroux and M. Mathieu (157 a), E. Heuser and H. Charbonnier (157 b), and by J. J. Stöckly (157 c), however, indicate that, in concentrated solutions, the cellulose xanthate molecules can neither be regarded as "free" in the sense of an individual mobility nor as persistent aggregates built up by macromolecules with permanent junction points. The picture

of the solution state can be regarded as a statistical binding and releasing of the junction points where one macromolecule may belong to several cohesion regions.

The state of cellulose in solutions has been extensively treated in a recent monograph by P. H. Hermans (157 d).

The examples of rubber and other substances which consist of long-chain molecules which have been coiled up but which form a crystal lattice when the molecules are stretched, has led to the supposition that such an effect may occur when hydrate cellulose is extended, the quantity of crystalline material increasing at the expense of the amorphous regions (158). O. Kratky and A. Sekora (158 a) employing the X-ray method mentioned above for determining the quantity of crystalline material, have found that when Hermans' hydrate cellulose filaments (158 b) are stretched, or when the filament is shrunk, or both, the amount of crystalline material in the fiber does not change. An effect like that in rubber does not occur. The quantity of crystallites formed during the regeneration of hydrate cellulose from the viscose solution does not change.

This result agrees with those of recent investigations by E. L. Lovell and O. Goldschmid (159). They found that the degree of crystallinity of various viscose fibers, determined by Nickerson's method (139), did not depend very much upon the degree of stretching, or on the crystallinity of the cellulose from which the viscose was derived, but chiefly upon the conditions under which the viscose was coagulated (or the cellulose regenerated). W. A. Sisson (160) has given an excellent review of this subject.

H. Staudinger, P. Herrbach, and H. Stock (161) have recently observed that the triacetates of native celluloses are insoluble in organic solvents like *m*-cresol and chloroform, while the triacetates of reprecipitated celluloses swell and go into solution. They also found that when cotton is xanthogenated to fiber xanthogenates, and the cellulose then regenerated and acetylated, an acetate results which is practically insoluble in organic solvents. But if the fiber xanthogenate is dissolved and the cellulose regenerated from *dilute* solution, and then acetylated, a soluble acetate is obtained. When the cellulose is regenerated from concentrated solution, the solubility is much lower—the product from a 20% solution, for example, is only 16% soluble. Oddly enough, a flax cellulose regenerated from a 1% solution gave an acetate which was scarcely soluble.

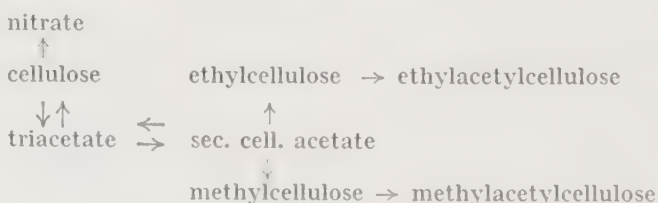
From this circumstance it was concluded that there are differences in structure between the celluloses of different plants, and that it was not impossible that "every plant produces its own characteristic cellulose."

The difference between native and regenerated cellulose lies presumably in the difference in arrangement of the cellulose molecules in the solid fiber, rather than in the presence of foreign substances or of cross-linkages.

II. Staudinger (162) advanced the point of view which regards cellulose in solution as a linear colloid; in other words, the cellulose is considered to be a molecular filament, stretched out lengthwise, and unbranched. This conception is rooted in the observation that all celluloses, no matter what their molecular weights, obey the same viscosity law. Hence the structure must be the same in the whole series of cellulose polymers, from those with an average degree of polymerization (D. P.) equal to 20 to those with a D. P. of 3,000 or more. The stretched out, unbranched nature of the cellulose chains is also supported by X-ray data and by the fact that the K_m constants of high-polymeric cellulose acetate agree well with those of the oligosaccharide acetates. (For the definition of K_m , see p. 68.)

Cellulose esters or ethers in organic solvents give monomolecular solutions, according to H. Staudinger (163).

Staudinger points out that the existence among the oligosaccharides of molecules in which three, four, or five glucose residues are joined by primary valences is proved by the fact that these saccharides can be esterified or etherified without changing their degree of polymerization. The high-molecular polysaccharides like cellulose can likewise be converted to products with the same degree of polymerization. Staudinger has succeeded, for example, in converting cellulose into acetates and nitrates, and has recovered the original cellulose by saponification of the acetates. The acetates can also be converted into analogous polymeric ethers. The molecular weights of the esters and ethers were determined by the osmotic method. The transformations of the analogous polymeric cellulose derivatives are summarized in the following scheme:



An example of the values obtained is given in the following tables:

Degree of Polymerization

Celluloses	Triacetates	Cellulose from the Triacetates
500	505	490
790	795	780
1,000	970	955
1,570	1,670	1,680

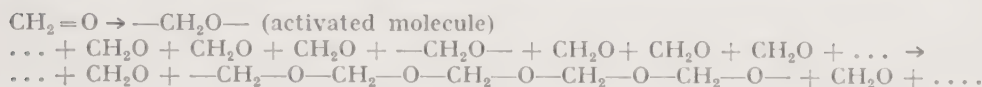
Analogous Polymeric Cellulose Derivatives

Triacetates	Cellites	Methylcelluloses	Methylacetylcelluloses
165	165	160	165
185	185	170	210
206	205	210	195
390	393	410	425

It is, according to Staudinger, unthinkable that cellulose compounds could exist in solution in micellar form, for micelles cannot undergo such chemical transformations without being opened up, which would result in great changes in the size of the micelles.

A similar conclusion has been drawn by O. Kraemer (164), who performed reversible acetylations of cellulose to the di- and triacetates and found that the degree of polymerization was not changed during these transformations.

Staudinger (165) also succeeded in quite a different way in showing that synthetic compounds with a chain-like structure behave like cellulose. The polymerization of formaldehyde, for example, results in the formation of homologous polyoxymethylenes having identical structural units:



This is an example of a chain reaction, which can lead to high-polymeric, viscous compounds. The chain reaction is finally stopped in one way or another. Under suitable conditions the resulting products have an extremely high molecular weight. A degree of polymerization of not less than 100 was established, and it is noteworthy that polyoxymethylenes with a fibrous structure finally appear. This was the first synthetic organic fiber. The colloidal nature of the solutions of this substance are caused, according to Staudinger, not by the formation of micelles, but by the size of the molecules (166). In other words, the length of the chain, consisting of atoms held together by primary valences (covalent bonds), is so great that it attains colloidal dimensions. Staudinger made the very important discovery that there is a direct connection between the length of the chain and the viscosity of the solution.

The viscosity of solutions of spherical molecules is, according to A. Einstein (167) independent of the particle size:

$$\frac{\eta_{sp}}{c} = 0,0025 \ s$$

$$\eta_{sp} = \text{specific viscosity} = \eta_{rel} - 1$$

η_{rel} = relative viscosity = $\frac{\eta}{\eta_0}$ (η = viscosity of the solution, η_0 = viscosity of the solvent)

c = concentration in g./l.

s = specific gravity of the solute

Stretched-out, chain-like molecules behave differently. In this case the viscosity number $\frac{\eta_{sp}}{c}$ should be proportional to the degree of polymerization P , according to Staudinger (168).

$$\frac{\eta_{sp}}{c} = K_m P, \text{ or rather } \lim_{c \rightarrow 0} \frac{\eta_{sp}}{c} K_m P$$

Here K_m is a constant characteristic of the particular homologous polymeric series and of the solvent (169).

The constant is determined for each homologous series of polymers by osmotic measurements. The values of K_m are all nearly equal in Schweizer's reagent, as the following figures show:

Substance	$K_m \times 10^4$
Cellulose.....	5.0
Xylan from straw and beech wood.....	5.0
Mannan from spruce wood.....	4.4
Salep mannan.....	4.4

One point is to be noted in this connection. The high-polymeric substances frequently consist of mixtures of different members of a homologous polymeric series. The determination of the molecular weight of such a polydisperse system (mixture of polymers of different molecular weight) yields an average value. Different mixtures with the same average degree of polymerization can have different compositions and therefore different properties.

The influence of the polymolecularity of rayon silk and rayon wool on the physical properties may be noted here. R. E. Dörr (170) and W. Schieber (171) have particularly called attention to this matter. J. Löbering (172) states that it is entirely proper to require that pulp for artificial silks have as low a degree of polydispersity as possible, and J. Kleine (173) emphasizes that experience has gradually made it more and more clear that the highest quality product is obtained in the viscose process when the best pulps are used, and that the removal of the wood ray cell leads to an improvement in the quality of the pulp. Cf. also W. Schieber (171). A. Zart (174) asserts that a high degree of polymerization is

favorable for many of the qualities, particularly the resistance to abrasion. According to Staudinger (175) a high degree of polymerization is not so important for the tearing strength, provided that a certain lower limit is exceeded. A. M. Sookne and M. Harris (175 a) found that the mechanical properties of fractions of cellulose acetate were highly dependent on the molecular weight, when the degree of polymerization was below 200. The strength characteristics of fractions which had a degree of polymerization above 200 were practically constant.

O. Eisenhut and E. Kuhn (176) report that artificial cellulose fibers are composed of fibrils, just like the natural ones. The natural fibers have very uniform fibrils, lying parallel, and firmly joined together; this is the reason for the excellent properties of the natural fibers. Degradation results in a weakening of the bonds. Fibers produced by artificial spinning have fibrils of various strengths, held together more loosely. Slow coagulation during the preparation of the fibers results in the formation of fibrils similar to those of the natural fibers. Treatment with formaldehyde strengthens the cohesion of the fibrils in artificial fibers, but increases the brittleness of the fibers. According to L. M. Welch, W. E. Roseveare, and H. Mark (176 a), rayon filaments are easily broken down into fibrils after swelling in seventy per cent nitric acid. Only rayons having high crystallite orientation separate into fibrils, whereas unoriented rayons do not.

Determinations of the average degree of polymerization by the osmotic and viscosimetric methods yield different results, which diverge more, the greater the dispersion of the chain lengths. The reason for this is that in the osmotic method the smaller molecules have the greatest influence, while the highmolecular portions have most influence on the viscosity. This naturally affects the value of the constants K_m (177).

The K_m values given are correct only for mixtures from which the largest and smallest molecules have been removed. Polydisperse mixtures are formed by the degradation of native cellulose. Technical pulps and rayon silk constitute such mixtures.

The polymolecular nature of such mixtures can be demonstrated by fractional solution or fractional precipitation. A fractionation can also be effected by means of an ultracentrifuge (178).

The simple relationship between the viscosity and the degree of polymerization given above assumes that the solutions are so dilute that the dissolved molecules have no interaction with each other. Staudinger has termed such solutions "sol solutions", in distinction to "gel solutions." The relationship between viscosity and molecular weight is more complicated in the case of the latter (179).

It is therefore important to know the concentration below which the solution may be considered to be a sol solution. This concentration is termed the limiting concentration. For cotton cellulose with a degree of polymerization of 2,000, it is 0.085 %, while the limiting concentration of a cellulose dextrin with a polymerization of 10 is 17 %. No sharp boundary exists between sol solutions and gel solutions.

The determination of molecular weights by the *osmotic-pressure method* is based upon the equation

$$M = \frac{RTC}{P}$$

where C is the concentration of the solute and P the pressure. For thread-shaped molecules like cellulose derivatives the quotient P/C increases with the concentration and has to be determined by extrapolation to the concentration $C = 0$. It is not yet quite clear how this extrapolation is performed best. A review of osmotic measurements on cellulose derivatives has been published by A. J. Stamm (180).

The osmometers hitherto used for the determination of molecular weights of high polymers are based on the common principle of a length measurement (difference in meniscus height between solution and solvent). The lowest height difference which can be measured is of the order of 0.1 mm. T. Svedberg (181) proposed weighing the amount of liquid which corresponded to the height difference, in order to obtain greater accuracy. I. Jullander (182, 183) in Svedberg's laboratory, therefore constructed the so-called "osmotic balance" which theoretically should be able to determine a height difference of 0.001 mm. He thus made it possible to carry out measurements at a lower range of concentration. Certain sources of experimental errors reduce the theoretical degree of exactitude to some extent. The values for the molecular weights M_n of nitrocelluloses given in the table on p. 73 are calculated from measurements carried out with the osmotic balance.

From Fig. 42 it becomes clear, that Jullander (182), measuring M_n of nitrocelluloses with the osmotic balance, was able to use lower concentrations than had been possible previously. An improved osmotic balance has been described by B. Enoksson (183 a).

At the beginning of the thirties investigations on the cellulose molecule were made with the aid of the *ultracentrifuge* (184) by A. J. Stamm (185) and later by E. O. Kraemer (186) at T. Svedberg's laboratory at Uppsala. Only since the beginning of World War II has the ultracentrifugal study of cellulose and cellulose derivatives been taken up on a broader basis under the direction of T. Svedberg (187, 188, 189, 190, 191, 192). The

substances studied have mainly been cellulose dissolved in cuprammonium, and nitrocellulose.

Ultracentrifuge methods are useful both in the determination of average polymerization degrees and the distribution around these average values. Three different methods are used, namely (1) determination of sedimenta-

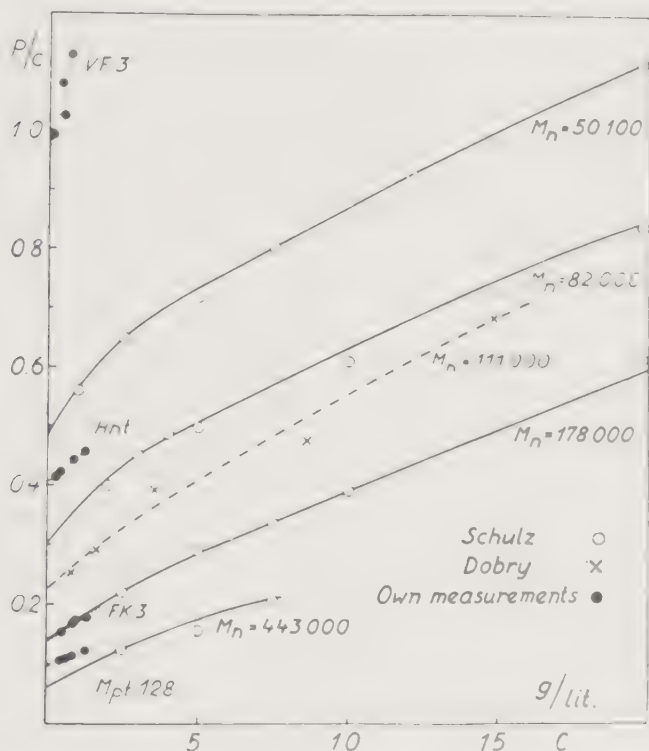


Fig. 42. Osmotic pressure measurements of nitrocellulose solutions by Schulz (acetone), Dobry (acetone), and Jullander ("own measurements") (butyl alcohol).

tion constants by measuring the *sedimentation velocity*, (2) determination of the *sedimentation equilibrium* from which molecular weights can be directly computed, and (3) determination of the *diffusion constant* D by measuring the diffusion.

In a sedimentation velocity experiment (1) a solution of the high polymeric substance is subjected to strong centrifugal forces. In a sedimentation equilibrium experiment (2) a much smaller centrifugal field is used and the centrifugation carried on until an equilibrium between sedimentation and diffusion has been established. Diffusion measurements (3) are, of course, carried out independently of the centrifuge and may be performed in different ways.

For the calculation of the molecular weight of cellulose and its deriva-

tives a combination of methods (1) and (3) is mostly used, and the molecular weight M is determined according to Svedberg's equation:

$$M = \frac{RT}{1 - V\varrho} \cdot \frac{s}{D}$$

where s is the sedimentation constant, D is the diffusion constant, V is the partial specific volume of the solute, ϱ is the density of the solvent, R is the gas constant and T is the absolute temperature. For the calculation of M an experimental value for V is then necessary. It is, generally, easy to obtain. The equation is valid only for infinite dilution, and therefore the values for s and D have to be obtained by extrapolation to zero concentration. For the sedimentation constant s this can be done in various ways with rather great confidence, while the determination of D at the concentration $\rightarrow 0$ still causes both theoretical and experimental difficulties.

Using the equilibrium method, it is possible to calculate the molecular weight from the equation

$$M = \frac{2RT \ln \frac{c_2}{c_1}}{(1 - V\varrho) \omega^2 (X_2^2 - X_1^2)}$$

where c_1 and c_2 are the concentrations at distances from the center of rotation of X_1 and X_2 , respectively, and ω is the angular velocity of the centrifuge. For the other symbols see the preceding equation. In this case it is not necessary to know the diffusion constant. This is, of course, an advantage; on the other hand, however, the time which is necessary for establishing the sedimentation equilibrium, is, in the case of thread-shaped molecules like cellulose, at least 10-14 days, which makes such a determination extremely tedious.

In the case of nitrocelluloses H. Mosimann (191) has further shown that the sedimentation-equilibrium method can be applied only at relatively low concentrations and moderate molecular weights. It cannot be used for cellulose derivatives with molecular weights higher than about 80,000, because of the deviations from simple thermodynamic laws in the case of such thread-like molecules.

It is obvious that a complicated substance like cellulose cannot be described merely by some kind of average value for the molecular weight. The ultracentrifuge methods, however, also give information about polydispersity. It can be obtained from the rate of widening of the boundary line between solvent and solution during a centrifuge run. This rate is defined as $\frac{dB}{dr}$, called the *widening value*, where B is the area under the

sedimentation curve divided by its maximum height, and x is the distance from the centrum of rotation. To give a value for the polydispersity, $\frac{dB}{dx}$ is extrapolated to zero concentration. From $\left(\frac{dB}{dx}\right)_0$ and the skewness of the sedimentation curve a frequency curve for the molecular weights can then be constructed. In order to fix the frequency curve along the molecular weight axis an independent value for the molecular weight has to be calculated, which is generally done on the basis of osmotic measurements.

N. Gralen (189) determined the molecular weights of cellulose and derivatives by sedimentation velocity and diffusion experiments. He found, that native fiber celluloses had molecular weights of the order of magnitude of $1.5\text{--}2 \cdot 10^6$, while wood celluloses, which had been isolated by chemical means, had lower molecular weights ($0.34\text{--}0.68 \cdot 10^6$). The highest molecular weight was found for the cellulose from flax fibers ($5.9 \cdot 10^6$). From attempts to extract the cellulose of wood directly with cuprammonium it appeared that the average molecular weight of cellulose in wood is at least $0.8 \cdot 10^6$. Thus, the sedimentation-diffusion method gave appreciably higher values than does Staudinger's viscosity rule.

Jullander (187) compared the molecular weights obtained in different ways for various samples of nitrocellulose. M_n is the average value obtained from osmotic-pressure measurements (*number average*), M_w (*weight-average*) and M_z (*z-average*) are values obtained either from sedimentation-equilibrium or from sedimentation-velocity plus osmotic-pressure measurements, $M_{w,w}$ are values from sedimentation-velocity plus diffusion experiments, and M_v values from viscosity determinations. Jullander's values are given in the following table:

Molecular Weights of Nitrocelluloses

Sample	Molecular weight $\times 10^{-3}$				
	M_n	M_w	M_z	$M_{w,w}$	M_v
e. h.	165	—	—	267	220
V F 120.	57	87	116	91	77
V F 3.	25.3	19.1	47.9	27.8	31.6
V F $1\frac{1}{2}$	13.3	17.9	21.8	13.8	17.0
Lnt.	86	141	247	153	143
Hnt.	60	—	—	100	96
Mpt 128.	258	386	—	495	344
A F 1.	16.8	22.7	42.8	16.3	22.4
F K 2.	162	231	317	268	195
F K 2 a.	—	—	—	—	186
F K 3.	182	272	266	282	295
F K 3 a.	—	—	—	—	186
F K 6.	133	151	168	186	149
F K 9.	444	—	—	1,175	530

Theoretically M_w and M_v should be identical. For six of nine nitro-celluloses in the table the ratio $\frac{M_w}{M_v}$ is between 0.98 and 1.16, with molecular weights ranging from 18,000 to 400,000. According to Jullander "this might be taken as evidence that the simple method of Staudinger for determination of molecular weights is quite applicable to nitrocellulose within a large range of the molecular weight." The values for $M_{w,w}$ however, seem to be too high. Furthermore, the quotient $\frac{M_{w,w}}{M_n}$ seems to increase with the molecular weight. The molecular weight values previously reported by Gralén (189) and by Gralén and Rånby (190) might therefore be too large. The reason for this is probably to be found in the practical and theoretical difficulties encountered in the determination of the diffusion constant D .

A similar conclusion was drawn by O. Bryde and B. Rånby (192) in their investigations concerning the molecular weight and other properties of "native wood cellulose." These authors studied nitrated celluloses which had been prepared under mild conditions from spruce wood. The following table shows figures for the degree of polymerization in various samples (P_v determined from viscosity, $P_{w,w}$ from sedimentation-velocity plus diffusion, P_n from osmotic measurements):

Molecular Weights Determined by the Different Methods

Sample No.	Lignin Content %	P_v	$P_{w,w}$	P_n	$\frac{P_{w,w}}{P_v}$
Wood	27.4	1,620	1,030	—	0.64
2/145	23.2	3,010	3,770	—	1.25
4/132	22.2	3,060	24,450	—	8.00
7/120	19.6	3,220	7,610	1,160	2.36
7/132	18.3	3,070	4,120	—	1.34
3.5/145	14.6	2,840	9,780	—	3.44
24/120	8.6	2,930	5,340	—	1.82
35/120	7.8	2,850	2,100	590	0.74
10/132	7.1	3,000	3,720	—	1.24
8.5/145	2.0	845	630	—	0.75

A comparison of the different values of P indicates immediately the presence of serious discrepancies. The reason for those must, according to Bryde and Rånby, be sought in the diffusion measurements. A critical discussion of the different methods leads these authors to the conclusion that native wood cellulose has a weight average degree of polymerization of about 3,300, which corresponds to a molecular weight of a little more than 500,000.

Concerning the polydispersity of cellulose, Gralén (189) found that there is a general tendency toward increasing polydispersity with increasing

molecular weight. Wood cellulose is more heterogeneous than fiber cellulose. The alkaline depolymerization involved in the viscose process increases the polydispersity.

Jullander (182) determined the molecular weight distribution in various nitrocelluloses with the aid of his "three parameter method" and found that the curves had one maximum and a positive skewness. He also determined the polydispersity from measurements of $\left(\frac{dB}{dx}\right)_0$.

This short review of the work done by the Uppsala school may be concluded with a quotation from T. Svedberg (183): "The thread-like shape of these molecules and the polydispersity of cellulose solutions cause, however, great experimental and theoretical difficulties. The sedimentation technique as well as the diffusion and osmotic-pressure measurements have to be pushed to the utmost degree of perfection in order to give satisfactory data."

In 1943 and 1944 P. Debye (193) showed that the measurement of *light scattering* in a solution of a high molecular substance can be used as an absolute method for the determination of weight average values for the big molecules. Further investigations in this field have resulted in a development of the method, which now also permits one to calculate the shape of the molecules and furthermore—if certain conditions are fulfilled—to construct the molecular weight distribution curve for the dissolved polymer.

Cellulose acetate in acetone solution has been investigated by Stein and Doty (194). They used four fractions, the molecular weights of which had been determined by osmometric, viscosimetric and ultracentrifugal methods. The following table contains the results obtained from light scattering measurements together with the osmometrical values:

Molecular Weight Data on Cellulose Acetate

Fraction	Light Scattering Method			Osmotic Pressure Method
	Uncor.	Cor. for Depolarization	Cor. for Dissymetry	
8 B.	118,000	114,000	173,000	163,000
23 B.	92,000	88,700	135,000	133,000
18 B.	60,000	55,600	77,000	75,000
32 B.	47,000	43,000	60,000	65,000

The final corrected values are in good accordance with the osmometric values.

A review on "Light Scattering in Polymer Solutions" has been given by H. Mark (195).

Quite divergent views are held as to the *shape of the cellulose molecules in solution*. Staudinger considers them to be rigid, elastic rods, while

O. Kratky and H. Mark (196) think that they have a serpentine form. W. Kuhn speaks of coiled and flexible chains (197), and F. H. Müller (198) also assumes that the linear molecules are coiled in solution, but not so tightly as Kuhn has calculated; Müller also believes that the molecules uncoil somewhat at low concentrations (sols). O. Kratky (199) emphasizes that the molecules can only crystallize in the stretched-out condition, and that if the tendency toward coiling is great, amorphous substances will result. If the tendency toward crystallization prevails, micellar systems are formed; and the agglomeration of the molecules finally leads to the formation of fringe micelles. The ends of molecules which protrude from the fringes can be incorporated into neighboring micelles, and systems arise which are like those shown in Fig. 40, p. 57.

In accord with his idea that cellulose is built up of fringe micelles, and goes into solution as such in viscose, W. Schramek believes that on coagulation the micelles are joined together by an interlocking of the fringes brought about by van der Waals' forces. This would form a solid system with alternate crystalline and amorphous regions, which would be considerably less compact than the system shown in Fig. 40, where the crystallites are held together by primary valence chains. [The smaller wet strength of regenerated cellulose could be understood in this way, since the interlocked fringes could be much more easily loosened than the primary valence chains traversing the different regions. Cf. W. Schramek, U. Metzner, and E. Seidel (200). The results of studies on the behavior of cellulose in viscose solutions, however, including especially the experimental findings of Hermans, make it improbable that Schramek's conception corresponds to the actual situation].

H. Mosimann (201) investigated the sedimentation in the ultracentrifuge of nitrocellulose fractions having molecular weights of 6,200 to 613,000. The sedimentation constants depended very much upon the concentration, as had been found in earlier work on filamentary molecules. The ratios of the axes, determined by various methods, were compared with one another and the conclusion was drawn that the nitrocellulose of lower molecular weight was stretched out in solution, while that of high molecular weight was more wavy in form. Coiling was out of the question. N. Gralén (189) and I. Jullander (182) come to the same conclusion; the cellulose chains are not branched, and they are only slightly waved. T. Neubauer (202) showed by calculations of the light scattering by cellulose solutions that the cellulose is present in the form assumed by Staudinger.

I. I. Hermans (203) concludes from the behavior of cellulose in diffusion and sedimentation, that randomly coiled structures may occur.

B. CHANGES OCCURRING IN CELLULOSE BY SWELLING, CHEMICAL AND ENZYMIC ATTACK, HEAT, AND MECHANICAL TREATMENT

1. Hydrate Cellulose. Swelling occurs when native cellulose is treated with concentrated aqueous solutions of electrolytes. Either intermicellar or intramicellar processes may be involved, according to J. R. Katz (204). If the changes are intermicellar, the X-ray diagram is not affected; this is the case when cellulose is swelled by dilute salt solutions. With other solutions the swelling proceeds farther, and the interference pattern is altered. The product formed in the latter case is known as "hydrate cellulose."

The swelling caused by the action of sodium hydroxide on cellulose has been studied most thoroughly (205). The so-called mercerization of cellulose should be mentioned here. It is probable that there are several intermediate stages in this process, and that the reaction proceeds through the formation of compounds of the cellulose with the swelling agent (206). This is true not only of the swelling with bases, but also of that with acids (207). When cellulose is dissolved in strong acids (HCl , H_2SO_4 , HNO_3 , etc.), hydrate cellulose is formed first. Even at moderate concentrations of the acid the reaction is chiefly intermicellar, and the lattice is affected only when a certain concentration has been reached. The action of nitric acid on cellulose may be mentioned as an example. The intramicellar reaction sets in when the HNO_3 concentration exceeds 61 %, and Knecht's compound $\text{C}_6\text{H}_{10}\text{O}_5 \cdot \text{H}_2\text{O} \cdot \text{HNO}_3$ is formed.

Cellulose precipitated from solutions also consists of hydrate cellulose. The artificial silks and cellulose films prepared by various procedures belong to this class of substances. Particularly intensive studies have been made of the hydrate cellulose obtained by the action of sodium hydroxide (208). X-ray investigations have shown that sodium hydroxide does not cause any change on the X-ray pattern until the concentration reaches 8 or 9 per cent. At lower concentrations 1 mol. of NaOH reacts with 2 glucose units in a "pseudostoichiometric" reaction on the micellar surface. When the NaOH concentration is 13-19 %, one mol. of NaOH is taken up for every glucose unit. This causes a change in the X-ray diagram, and it is assumed that sodium ions are inserted between the chains (alkali cellulose I, Fig. 43). The X-ray diagram is changed again when the concentration of NaOH exceeds 20 % (alkali cellulose II). When the sodium cellulose is dried, the alkali cellulose III is formed. If the alkali celluloses are treated cautiously with water and the sodium ions thus displaced by water molecules, a water cellulose (IV) is formed, which goes over into hydrate cellulose on being warmed.

Hydrate cellulose can be converted to native cellulose by heating to temperatures between 140 and 300° C with glycerin, or with water under pressure (209).

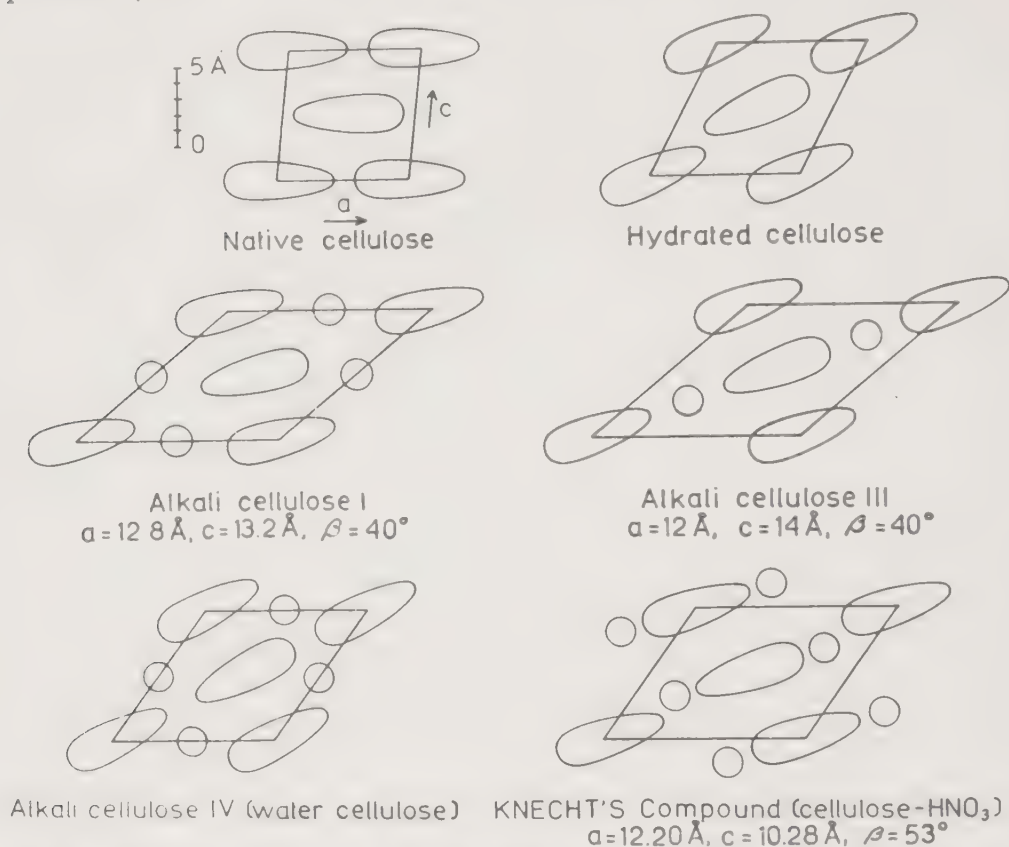


Fig. 43. Schematic projection of cellulose chains on the *ac* plane. The glucose rings are shown as ovals, and the reagents which have entered the structure are represented by the circles.

2. Hydrocellulose. When cellulose is treated with dilute mineral acids, either for a long time in the cold, or for a shorter period with warming, the mechanical strength of the fibers disappears, and they disintegrate into a powder. This powder is called *hydrocellulose*. This substance has been the subject of numerous investigations (210), but its chemical nature has not yet been fully elucidated. It is very probable that hydrocellulose is not a single chemical substance, but a mixture of several substances. Some authors are of the opinion that it consists of a mixture of unchanged cellulose and its degradation products (211). The principal constituents may be separated by treatment with alkali, which yields a residue of unchanged cellulose. The solution, however, does not contain a single substance, but rather several different ones. R. O. Herzog (212) found that hydrocellulose obtained by the action of hydrochloric or sulfuric

acids on cellulose gave the same X-ray diagram as the original cellulose. He believes that the reducing power of hydrocellulose is the result of impurities. E. Knoevenagel and H. Busch (213) established the important fact that the hydrocellulose is soluble in alkali, and that it can be precipitated from the solution. They called this substance "alkali-soluble cellulose." K. Hess and his coworkers advanced our knowledge one step further by showing that alkali-soluble hydrocellulose is not amorphous. Polarimetric measurements have further shown that hydrocellulose which has been sufficiently purified by reprecipitation gives the same rotation in cuprammonium solution as does unchanged cellulose (214). Hess has termed this alkali-soluble cellulose "Cellulose A." According to him, the alkali solubility is not due to chemical causes, but rather to "changes in the physical state" (215). T. Lieser (216) thinks that cellulose begins to dissolve in dilute alkalies when it has lost its micellar structure. This loss of structure can occur without breaking the cellulose chains.

A somewhat similar theory has recently been presented by L. A. Hiller and E. Pacsu (217). Their theory claims that weak acids, used in the preparation of hydrocellulose, do not hydrolyze 1,4-glycosidic bonds, but rather hydrolyze hemiacetal bonds which connect the primary chain molecules together to give rise to secondary chain molecules. Simultaneously, low molecular substances like glucose and cellobiose—one molecule for every 548 glucose-anhydride units—are leached out.

M. Lüdtkke (218) is of the opinion that the brittleness of the fibers which is observed after attack by mineral acids is due to the fact that the material of the primary lamellae and of the "cross structures" is attacked, causing destruction of the "skin substances" which hold the fiber together. H. Hess (219) has adopted this point of view, and thinks that the strength of the fibers is not due to the mechanical properties of the interior substance but to those of the enveloping system. Hence it is possible to reduce the strength very markedly without disturbing the crystallites, simply by destroying the enveloping system. This occurs when hydrocellulose or oxycellulose is formed. There are no experimental proofs of these conceptions; indeed, it is not even known what substance the enveloping system is made of, how it is distributed in and around the fibers, or whether it is really of any importance at all.

A somewhat similar view has recently been expressed by C. W. Hock (124 b). On the basis of microscopic and electron-microscopic studies, this author suggests that the crystalline component of native fibers is located principally within the fibrils, while the interfibrillar regions, and possibly the fibril surfaces, consist mainly of amorphous cellulose. These amorphous regions are more easily degraded by hydrolytic agents than the fibrils

themselves. This view diverges from the more generally adopted one, according to which the amorphous regions are located within the fibrils alternating there with the crystallites.

H. Staudinger and M. Sorkin (220) strongly emphasize the fact that the changes which occur when native cellulose is treated with acid are due solely to the glucosidic hydrolysis of the long cellulose chains. They investigated the change in the average degree of polymerization of the cellulose when raw cotton was treated with 1 N acids at 53°C for a long time. The results are represented graphically in Fig. 44.

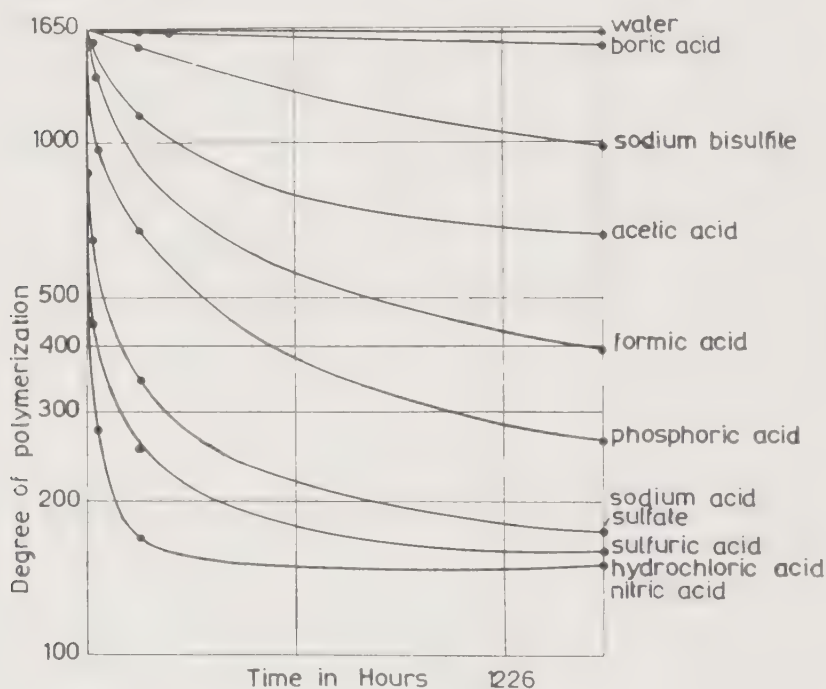


Fig. 44. Change in the degree of polymerization of cotton on treatment for various lengths of time with 1N acids.

The speed of degradation obviously depends directly on the hydrogen ion concentration of the solution. It is seen that the degradation seems to stop when the degree of polymerization has decreased to one tenth of the original value, *i.e.*, when only relatively few of the links of the chain have been broken. The speed of degradation is also proportional to the number of glucose linkages present, as is the case with the hydrolytic degradation in homogeneous systems and with the oxidative degradation. (221).

In the hydrolytic-oxidative treatment of cotton linters used by R. F. Nickerson and J. A. Habrle (140) for the determination of crystalline and amorphous parts in cellulose materials (*cf.* page 61), the degree of

polymerization, measured by the viscosity method, dropped rapidly from an initial value of 1,760 to 274 and then remained constant. It was assumed that these chain lengths correspond to the length of the crystallites. A similar level was obtained in the mild hydrolysis experiments reported by O. A. Battista and S. Coppick (222) and extensively discussed by E. Pacsu (223).

W. N. Haworth, S. Peat, and W. J. Wilson (224) determined the chain lengths of hydrocelluloses which had been prepared by the action of 5% hydrochloric acid on cotton, and found values which corresponded to 70-200 glucose residues.

The determination of aldehyde groups liberated during acid degradation has also been used to study the extent of degradation (225). The values obtained by this method compare well with those obtained by the viscosity method.

It has long been known, and it has already been mentioned that the strength of the fibers is tremendously decreased at a particular stage of the action of acids. Investigations of this matter were carried out in the work of Staudinger and Sorkin mentioned above. The values of the strength characteristics—folding endurance, breaking load, and extensibility—were not proportional to the degree of polymerization, but were more complicated functions of the polymerization. In the case of cotton fibers the strength characteristics did not change when the degree of polymerization was decreased from 1,650 to 700, but as soon as the degree of polymerization sank below 600 the strength was markedly affected, and it dropped to zero when D. P. reached 200.

According to D. A. Clibbens and B. P. Ridge (226) a linear relation between the strength characteristics of hydrocellulose and the fluidity of its solutions exists during a certain period of the degradation.

A. Bujewskoi (227) found that water-soluble hydrocellulose preparations gave 100% of glucose on hydrolysis with dilute mineral acids, while "amyloid" preparations yielded only 10% of glucose, and those with a molecular weight of about 11,000 gave only 20%. This might indicate that the hydrolysis can be carried out as a homogeneous reaction only when all the linkages are equally accessible to the reagent.

3. Oxycellulose. The reaction products obtained by oxidation of cellulose by any means whatsoever are known as oxycelluloses (228).

Pure cellulose in the form of paper or webbing is oxidized only extremely slowly by the air, for the strength apparently remains unaltered for long periods of time. H. Staudinger and F. Reinecke found (229) that linen, cotton, and paper celluloses are extensively decomposed only after several

thousand years. The cellulose of cotton cloth which was about two thousand years old had an average degree of polymerization of about 200. At this stage the fibers easily crumble to dust.

The velocity of the oxidative degradation of cellulose by the air was studied by O. Eisenhut (230), who used alkali cellulose as a starting material. It should be noted that the oxydation of cellulose by atmospheric oxygen is tremendously accelerated by the presence of alkali.¹

The consumption of oxygen per unit time is constant, as Eisenhut showed, and is therefore independent of the extent of degradation. W. Weltzien and G. zum Tobel (231) found that about half of the oxygen goes to form carbon dioxide; according to Eisenhut, the formation of carbon dioxide also proceeds at a constant rate.

A constant rate of oxygen consumption is synonymous with a constant rate of cleavage of the glucose linkages, and Eisenhut, assuming that the number of linkages cleaved per unit time was small in comparison with the total number of linkages in the cellulose and degradation products, derived the following expression for the length L_t of the chain at time t , in terms of the original length L_0 , the number n of linkages split per unit time, and the original number N_0 of cellulose molecules:

$$L_t = \frac{L_0}{1 + \frac{nt}{N_0}}$$

The change in length therefore follows a hyperbolic curve. The same thing is true of the changes in viscosity and degree of polymerization, since these quantities are directly proportional to the length of the molecules, as has been shown above. The asymptotes of the hyperbolic curves obtained from Eisenhut's data did not coincide with the abscissa ($L = 0$) but lay 40 or 50 units higher. The following figures for $(DP)_t$ were obtained after allowance had been made for this fact (Time unit = time necessary to reduce the initial DP to one half):

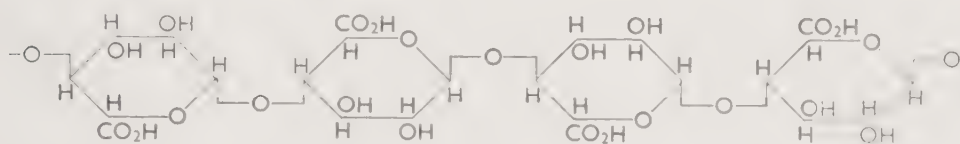
Time Units	$(DP)_t = kL_t$	
	Calc.	Obs.
0	860	860
1	430	425
3	215	190
7	107.5	120
15	53.75	60

The experiments of H. Staudinger and J. Jurisch (232) showed that extremely small quantities of oxygen are required to split a cellulose of a given D. P. into one with only half as great D. P. Cellulose dissolved in

¹ This point is of great practical importance in the viscose industry (231).

phosphoric acid was not appreciably attacked by the oxygen of the air, but if oxygen in the form of KMnO_4 solution was added, a mere four atoms of oxygen sufficed to split one mol. of cellulose with 1,000 glucose units into two mol. of oxycellulose with 500 glucose units each. This means that 160 kg. of cellulose with a D. P. of 1,000 can be converted into cellulose with a D. P. of 500 by $1\frac{1}{2}$ kg. of bleaching powder.

The degradation naturally depends upon the oxidizing agent and upon the speed of diffusion of the reactants. L. Kalb and F. v. Falkenhausen (233) obtained a uniform reaction on oxidizing cellulose with potassium permanganate after dissolving it in ammoniacal copper solution. Polyglucuronic acids were formed:



Nitrogen dioxide causes the same sort of oxidation, as has been demonstrated in several studies by W. O. Kenyon and his co-workers (234) and K. Maurer and G. Reiff (235). When cellulose is treated with an equilibrium mixture of NO_2 and N_2O_4 in carbon tetrachloride solution, the primary hydroxyl groups (in the 6-position) are oxidized to carboxyl. It is claimed that the "celluronic acids" formed arise by nitration of the primary hydroxyl groups, and subsequent oxidative denitration of the CH_2ONO_2 groups to carboxyl, by a process not further described.

Celluronic acids of the same type are obtained, although with somewhat lower yields, when a mixture of conc. nitric acid and nitrite, instead of nitrogen dioxide, is allowed to act upon cellulose (235 a).

It has been shown that celluronic acids are absorbed by body tissues without untoward effects. They are therefore used in surgery as absorbable packing. They have further been found to possess hemostatic properties (235 b).

Cellulose can also be oxidized in another way. D. A. Clibbens and B. P. Ridge (226), G. F. Davidson (236), and H. Staudinger and E. Roos (237) have demonstrated that secondary alcohol groups can be oxidized. The chain is not shortened in this process. In the oxidation of cellulose with periodic acid described by E. L. Jackson and C. S. Hudson (238) the glucose residues are split between carbon atoms 2 and 3, with the formation of two aldehyde groups. The polymeric aldehyde was hydrolyzed to glyoxal and D-erythrose. Oxalic acid was also formed, though in small quantities.

The oxidation of cellulose with periodic acid and metaperiodate was studied later by Davidson (239) and by H. A. Rutherford, F. W. Minor,

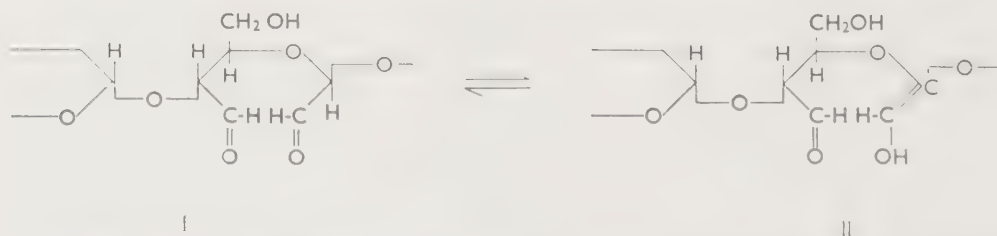
A. R. Martin and M. Harris (210), L. T. Heidt, E. K. Gladding and C. B. Purves (211) discussed some physical properties of periodate and lead tetraacetate, which they believe to be essential for the dialdehyde-cleaving activity of these oxidants. On the basis of these properties they decided that sodium perbismuthate, NaBiO_3 , and the hydrated, unstable Ag^{+++} ion also should be able to produce the dialdehyde cleavage. This conclusion was confirmed by experiments.

G. Jayme, M. Sätre, and S. Maries (212) succeeded in obtaining the polymeric aldehyde in nearly 100 % yield by using a buffered solution of periodic acid. It was also found that xylan gave a corresponding aldehyde.

Oxycelluloses of the aldehyde type reduce Fehling's solution; hence they can be further oxidized, and give high copper numbers. (This means that the copper number cannot be used to give an immediate value of the chain length. A cellulose with a high copper number does not necessarily consist only of short chains, but a high copper number does mean that the cellulose is of little value for technical purposes, either because it is much degraded, or because it contains many faults.) The chains can be broken at the oxidized points or faults by solution in alkali, e.g., in Schweizer's reagent. The chain does not disintegrate on nitration, however, and the nitrocelluloses so obtained give much higher viscosities than the cellulose dissolved in ammoniacal copper solutions. The following figures may be quoted from H. Staudinger and K. W. Eder (243):

DP from Viscosity of Cellulose	DP from Viscosity of Nitrate	% Difference in Chain Length	Cu No.	DP from Cu No.
280	1,500	435	3.1	25
275	900	225	2.7	29
190	730	280	5.5	14
130	460	250	12.4	6

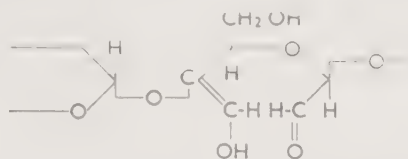
E. Pacsu (244) has tried to explain the above-mentioned alkali sensitivity of the dialdehyde type of oxycellulose. He points out that groups of type I in the presence of alkali may rearrange to the tautomeric form II:



The tautomeric form II represents an acetal of hydroxyketene, and it is known that such acetals are hydrolyzed by alkali.

An alternative explanation can be based on the work of W. L. Evans and

co-workers (245) who showed that enol-glycosides are alkalisensitive. An acetal of that type (III) could also be formed from I.



III

Model experiments by F. S. H. Head (246) seem to make the second alternative very probable.

A possible explanation for an alkaline cleavage of oxycelluloses with aldehyde groups in the 6-position of the glucose anhydride rings has been discussed by T. Bergek, S. Gustavsson and E. Lindvall (247).

G. Goldfinger, H. Mark, and S. Siggia (248) investigated the kinetics of the sodium periodate oxidation of cotton linters or of cellulose regenerated from ammoniacal copper solution. The oxidation of the glucose residues was shown to proceed in two steps, with the formation first of an aldehyde and then of a carboxyl group. M. Harris and his co-workers (249) had obtained similar results. The kinetics of both steps could be followed. The rate of the total oxygen consumption could be explained on the assumption that the cellulose contains both easily and difficultly attackable regions; these are probably the amorphous and crystalline regions of the cellulose (cf. p. 60).

Distillation of oxycellulose with hydrochloric acid according to the method of Tollens gives furfural and carbon dioxide. This is understandable, since glucuronic acid residues are present in the molecule. The reduction of Fehling's solution has already been discussed. This property is also characteristic of hydrocellulose. The formation of hydrazones can also be used for the detection of oxycellulose; hydrazinonaphtholsulfonic acid yields a hydrazone which can be coupled with diazobenzenesulfonic acid (249). The analytical determination of the groups characteristic for oxycelluloses, i.e., carbonyl and carboxyl groups, has also been studied by C. B. Purves and co-workers (250), and by E. Geiger (251), and recently by W. O. Kenyon and co-workers (234), and by K. Wilson (252).

According to A. Marschall (253), all degradation reactions which leave the structure of the fiber unchanged yield products which are soluble in formic acid-calcium chloride (or zinc chloride) mixture to the extent of only 10-20 %. The solution in calcium thiocyanate and sodium zincate is usually complete. The solubility in sodium hydroxide depends very much on the method of degradation; it is very great after oxidative

attack, but after hydrolytic splitting the products are only 5-6 % dissolved, even when the degree of polymerization is reduced to 250. It is best, therefore, to employ a formic acid-calcium chloride (or zinc chloride) solution for the recognition of the native character even of celluloses which have been extensively degraded. Mechanical degradation in an oscillating beater gives a product which is completely soluble in formic acid-calcium chloride, even at high degrees of polymerization, because as K. Hess and his co-workers have shown (254), the native structure of the fiber is completely destroyed by this treatment. Regenerated cellulose is likewise completely soluble in formic acid-calcium chloride.

The oxidations and degradations described above are of particular interest with respect to the various procedures for the bleaching of pulp. Those will be discussed in detail in Chapter VIII.

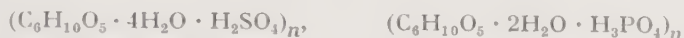
4. Degradation of Cellulose by Mineral Acids. Cellulose is brought into solution by mineral acids of certain concentrations; it is assumed that complex formation first occurs between the OH groups and the acid, and that the complex compound furthermore adds water molecules. Besides these reactions there is chemical breakage of the cellulose chain.

The degradation of cellulose by concentrated sulfuric acid has been studied in the greatest detail. B. de Carolles (255) was the first to investigate this "sulfolysis" carefully. He was able to show that the action of sulfuric acid gave rise to acids of various compositions, which were identical with the compounds which Braconnot had called "acide végéto-sulfurique." De Carolles named them "wood sulfuric acids." Purified wood cellulose was dissolved in sulfuric acid, and the solution diluted with water after various periods of time; the solution was neutralized with barium carbonate and then filtered, after which the filtrate was concentrated by evaporation and the salt precipitated with alcohol.

The barium salts so obtained had a constant ratio of BaO to SO_3 ; the ratio was 1 : 2. This was confirmed shortly thereafter by H. Fehling (256) and R. F. Marchand (257). Attempts were later made to isolate compounds of definite composition by fractional precipitation; this constituted an attempt to determine the steps of the sulfolysis and to explain the mechanism of the hydrolysis of these compounds (258). A. L. Stern (259) did indeed at first obtain a substance which was regarded as cellulose-disulfuric acid $\text{C}_6\text{H}_8\text{O}_3(\text{SO}_4\text{H})_2$. It gave on hydrolysis with acid a product with the formula $\text{C}_{12}\text{H}_{19}\text{O}_9\text{SO}_4\text{H}$.

G. Champetier and J. Bonnet (260) found that esterification with formation of a compound with the formula $\text{C}_6\text{H}_9\text{O}_4\text{SO}_4\text{H}$ occurs only when the sulfuric acid concentration is as high as 930 g. l. The yield was small.

A. af Ekenstam (261) also found that the sulfolysis begins with the formation of an addition compound of cellulose and sulfuric acid, similar to the compound with nitric acid which has been mentioned above under the name of Knecht-compound. Cellulose also reacts with phosphoric acid. The acid compounds have the following compositions, according to Ekenstam:



These compounds are soluble in the corresponding acids. The higher the molecular weight of the cellulose, the higher must be the acid concentration. The cellulose can be precipitated out of the solution again, and recovered quite free of acid. The compounds are thus completely hydrolyzed in water solution, and no stable sulfuric acid or phosphoric acid esters are formed under these conditions.

The behavior of acids during the solution of cellulose is noteworthy, according to Ekenstam. It turned out that high molecular celluloses are most easily saturated by acid of a certain definite concentration. In the case of phosphoric acid, this composition was $\text{H}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$. Ekenstam explains this by saying that under these conditions the above-mentioned addition compound $\text{C}_6\text{H}_{10}\text{O}_5 \cdot 2\text{H}_2\text{O} \cdot \text{H}_3\text{PO}_4$ is formed. At higher concentrations the saturation is evidently hindered by the formation of cellulose degradation products, and at lower concentrations the swelling is insufficient. Similar conditions hold in the case of sulfuric acid. The concentration of the acid which most easily saturates the cellulose is 57.6 %. The actual solution of the cellulose (which was cotton in this case) requires higher concentrations, viz., 65.4 % sulfuric acid and 82.9 % phosphoric acid. The greater the extent of the degradation of the cellulose, the lower is the concentration of the acid required (262). At lower concentrations of phosphoric acid the cellulose remains unchanged for a long time, and the solutions can thus be used for the determination of molecular weights (263).

The cellulose dissolved in mineral acids is degraded more or less rapidly, depending on the experimental conditions, giving glucose as an end product. The kinetics of this degradation have been investigated by various students.

K. Freudenberg and his co-workers (264) have studied the degradation with sulfuric acid quite carefully. They emphasize the fact that this process is not an ordinary hydrolysis, accelerated by hydrogen ions, but that the sulfuric acid molecules also play a part in the degradation. The reaction was followed by determining the aldehyde groups set free according to the Willstätter-Schudel method.

The speed of the degradation was also measured polarimetrically. It turned out that the linkages did not all react with the same speed. For

example, the unimolecular rate constant for cellulose was approximately 0.3 at the beginning of the reaction, and about twice as great at the end of the reaction. This fact was explained by the discovery that cellobiose, cellotriose, and cellotetraose are degraded more rapidly than cellulose. This led to the setting up of various hypotheses, including one to the effect that in every oligosaccharide one of the terminal linkages reacts with the speed found for cellobiose (K_2), and the other with the initial speed found for cellulose (K_n). The average velocity constant P between time 0 and time t was determined from the fraction of linkages split, α , at time t , making use of the equation

$$P = \frac{1}{t} \ln \frac{1}{1 - \alpha}$$

The following figures may be quoted for the calculated and observed values of α :

Cellulose Degraded in 51 % Sulfuric Acid at 18° C

Time in Min.	$P \times 10^4$	(1 — α), Determined by Titration	
		Observed	Calculated with $K_n = 0.305$ $K_2 = 1.07$
0	0.305	1.00	1.00
3,140	0.335	0.90	0.899
6,090	0.366	0.80	0.797
9,000	0.396	0.70	0.697
11,950	0.427	0.60	0.599
15,110	0.458	0.50	0.501
18,780	0.488	0.40	0.400
23,200	0.519	0.30	0.298
29,000	0.554	0.20	0.196
38,300	0.600	0.10	0.094
∞	0.665		

A. af Ekenstam, also making use of the same assumption, *i.e.*, that the velocity is proportional to the number of glucose linkages present at any given time, attempted to determine the reaction constants for the degradation of cellulose in phosphoric and sulfuric acids by measuring the change in the viscosity of the solution. The constants did not show any drift during the first part of the reaction when filter paper was used, but with cotton they were greater at the beginning of the reaction than later. Ekenstam attributed this to ester-like linkages in the cotton [cf. H. Staudinger (265), and K. Freudenberg and G. Blomquist (266)].

Measurements by G. V. Schulz and H. J. Lohmann (267) then have shown that cellulose becomes less and less uniform in composition during the hydrolysis with phosphoric acid. Consequently, the degree of polymerization determined viscosimetrically differs from the actual average degree of polymerization, and this discrepancy increases as the degrada-

tion proceeds (cf. p. 69). This change in the polydispersity of the cellulose renders the molecular weights determined by Ekenstam uncertain and explains the drift in the constants sometimes observed by him. In order to avoid this error Schulz and Lohmann determined the reaction rate constants as functions of the degree of polymerization, not carrying the reaction beyond the point at which the altered polydispersity begins to cause disturbances. The cellulose used must of course be as uniform as possible with respect to degree of polymerization, uniformity was achieved by saponification of the corresponding acetylcelluloses, which had been fractionated. It then turned out that the hydrolysis constants did not decrease when the degree of polymerization was carried from 1,500 to 130.

L. G. Sillén (267 a) has carried out interesting calculations concerning the course of chemical degradation of high-polymer chains. Some of his formulas, derived for the amount of polymer degradation products, the degree of splitting and the degree of polymerization, have previously been obtained in another way by W. Kuhn (267 b).

G. V. Schulz and E. Husemann (268) later published the results of measurements of the reaction rate constants for the hydrolytic decomposition in 13.1 *M* phosphoric acid of a series of cellulose fractions obtained by degradation. The measurements were made at 29° C. It turned out that the high-polymeric fractions contained linkages which were more rapidly split than the usual β -glucosidic ones. Only when the degree of polymerization fell below 500 did the easily-hydrolyzable linkages cease to occur in cotton cellulose. A closer examination of the constants reveals that they triple or quadruple in value when the DP decreases to about 20-60; this fact is explained on the supposition that not only the terminal glucose molecule but a whole group of molecules at the end of the chain is rapidly hydrolyzed. In order to explain the occurrence of rapidly hydrolyzable linkages Schulz and Husemann assumed that uronic acid residues are incorporated in the native cellulose chains, and that the number of carboxyl groups in the cellulose corresponds to the number of "faults" in the cellulose molecule. E. Husemann and O. H. Weber (269) reported that wood cellulose contains about four times as many carboxyl groups as fiber cellulose; this may be the reason, according to Schulz and Husemann, for the lower stability of wood pulp and wood pulp fibers as compared with natural fibers from cotton.

In later publications, G. V. Schulz (269 a) does not appear to maintain his previous view, that the easily hydrolyzable linkages correspond to uronic acid residues. In this connection, it also should be remembered that according to van der Wyk and Studer (97 a), native cellulose does not contain any carboxyl groups.

H. Sihtola's investigations of the speed of degradation of cellulose in zinc chloride solutions (270) confirmed the results of Schulz and Husemann. In that celluloses with a DP in excess of 500 were found to contain linkages which were more easily split than the 1,4-glucosidic linkages. The ordinary linkages are all cleaved with the same speed.

If the heterogeneity of the molecular weight distribution is measured as a function of the extent of degradation, it is found to increase much less rapidly than would result from random scission. G. V. Schulz (269 a) assumes that native fiber cellulose consists of β -glucosidic chains of uniform length (DP 3,200), which at regular distances of 500 glucose units contain some more sensitive linkage. It is further assumed that these sensitive bonds are oriented throughout the fiber in planes perpendicular to the fiber axis. This view is supported by electron microscopic examinations of wet-beaten and of hydrolytically degraded native fibers [E. Husemann and A. Carnap (270 a)]. Wet-beating gave long fibrils, whereas hydrolytic breakdown followed by mild mechanical treatment resulted in the formation of short, rod-shaped elements. The length distribution of these particles had a distinct maximum at 2,250 Å, which corresponds to 450 glucose units.

Similar particles have been observed by C. W. Hock (124 b) when cotton linters were boiled for two hours in solutions of 2.5 M HCl-0.6 M FeCl₃, previously used by Nickerson and Habrle (139, 140) in the oxidative hydrolysis of cellulose. The electron-microscopic picture of the hydrocellulose obtained in this way showed rod-shaped bodies which had a length of about 2,500 Å and a width of about 150 Å.

Recently, E. Paesu (271) came to the conclusion, that mild hydrolysis of cotton cellulose primarily results in the splitting of highly acid sensitive linkages, which are broken up more rapidly than the normal β -glucosidic bonds. He assumes that native cellulose possesses an indefinitely high molecular weight. In all the common procedures of preparing soluble cellulose derivatives, as for example nitration, an unintentional degradation to a DP of about 3,000 takes place. On mild acid hydrolysis, further highly sensitive linkages are broken up, and—without loss of substance—"limit cellulose" units, possessing a DP of 128 or 256, are formed. The few bonds, about 0.3 % of the total number of bonds, which are cleaved during these mild conditions, are assumed to be semiacetal or acetal bonds, originating from open chain glucose end groups of the "limit hydrocellulose" units and linking those together along the *a* and *b* axis of the fiber. A "laminated chain structure" would be the result of this kind of linkages.

As mentioned before (p. 81), Nickerson and Habrle (140), on hydrolytic breakdown of cotton cellulose, found a "limit DP" value of 274.

In contradiction to the above-mentioned authors, L. Jørgensen (138 b) could not find any support for the existence of periodic weak links in the cellulose chains of cotton. From hydrolysis experiments in homogeneous (phosphoric acid solution) as well as heterogeneous systems, he concludes that cotton is degraded by random splitting of the glycosidic links. In sulfite pulp, however, weak linkages seemed to be distributed rather frequently and at random over the fiber as well as over the single chains. Jørgensen suggests that anhydro-xylan units built into the anhydro-glucose chains may be responsible for these weak linkages. Finally, the behavior of an aspen pulp on hydrolysis seemed to indicate that it contained weak linkages distributed over the chain at more regular intervals.

As Jørgensen points out, it is obvious that further experimental evidence is required before making a selection between the two hypotheses, one of which postulates a regular and the other a random distribution of weak linkages.

The experiments of A. Banderet and B. Ranby (272) also seem to support the assumption of the presence of easily split linkages in the cellulose chain. They find that cellulose is degraded to a certain extent by the action of sodium hydroxide in spite of very careful removal of oxygen from the apparatus used.

According to T. Bergek (273), a "limit DP" value, 100-200, is also reached during the aging of alkali cellulose in the viscose process.

The limiting values, observed during the heterogeneous degradation of cellulose, may possibly find their explanation in recent experiments carried out by Ranby (274) in Syedberg's laboratory. When wood cellulose was hydrolyzed with boiling 2.5 *N* sulfuric acid, part of the resulting product could be peptized by washing thoroughly with water. In the colloidal solution thus obtained, the cellulose particles could be made visible by electron microscopy (Fig. 15). They were rod-shaped and of rather uniform size, having a length of approximately 500 Å and a width of 50-100 Å. They gave a sharp X-ray diffraction diagram, which indicates a high degree of crystallinity [Ranby and Ribi (124 a)]. Their length corresponds to the first maximum (DP about 100) of the ultracentrifugal frequency curves for different celluloses [B. G. Ranby (274 a), P. O. Kinell and B. G. Ranby (274 b)]. Their width is approximately the same as that of the fibrils observed after ultrasonic wave treatment of cellulose (cf. p. 57).

It is assumed by Ranby that these isolated colloidal particles are identical with the crystalline parts (crystallites, micelles) of the cellulose fibrils, which had previously been postulated on the basis of X-ray investigations. It is of interest to note that J. Hengstenberg and H. Mark (274 c) estimated the dimensions of the micelle in ramie, from X-ray data, to be approximately 50 Å in breadth and over 600 Å in length.

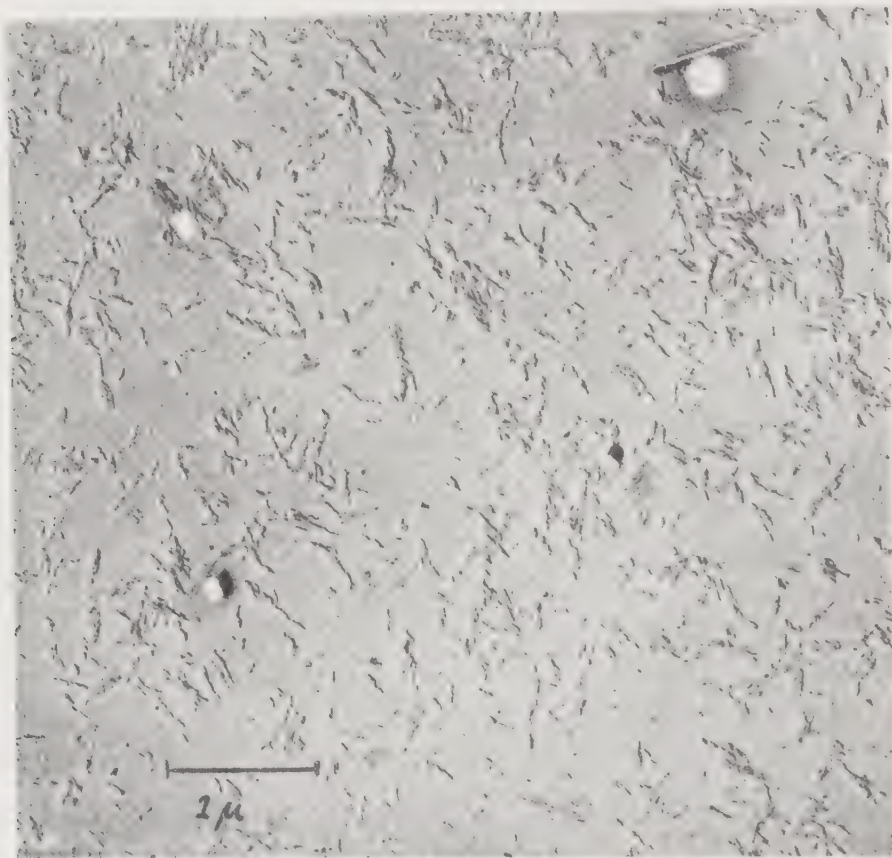


Fig. 45 Electron micrograph of micelles of mercerized wood cellulose, which has been hydrolyzed for 120 minutes with boiling 2.5 *N* sulfuric acid. Shadowed with gold-manganin.

The degradation of cellulose by the action of *hot, dilute mineral acids, for the purpose of saccharification*, has often been studied. E. Simonsen (275) made the first systematic investigation of this reaction. He determined the effects of temperature, reaction time, and quantity and concentration of the acid. The chief results of these studies are given in the following tables. The yield of sugar was determined by the reduction of Fehling's solution, and the figures checked by fermentation; approximate agreement was obtained.

Effect of Temperature (or Pressure) and of Acid Concentration.

40 g. Cellulose + 1,080 cc. Dilute Sulfuric Acid. Time: 4 Hours

Temperature Corresponding to a Pressure (in Atm.) of	Yield of Sugar in % of the Cellulose			
	0.15 % H_2SO_4	0.30 % H_2SO_4	0.45 % H_2SO_4	0.6 % H_2SO_4
1.3	—	2.5	2.7	3.1
2.1	—	6.6	8.6	10.6
2.7	—	9.3	11.3	12.6
4.0	—	16.4	—	20.3
6.0	21.5	28.0	30.7	43.9
8.0	30.5	38.4	45.0	33.3
9.0	—	43.1	—	—
10.0	35.0	36.6	30.0	18.6
12.0	38.4	—	—	—
14.0	20.0	—	—	—

*Effect of the Acid Concentration*40 g. Cellulose + Sulfuric Acid, Dissolved in the Following Quantities of Water:
Time: 2 Hours at 8 Atm. Pressure.

Quantity of Water in g.	Acid Concentration in %	Yield of Sugar in % of the Cellulose
250	1.5	18.4
500	0.75	35.0
1,080	0.44	45.4
1,500	0.23	32.5

Effect of the Time

40 g. of Cellulose + 250 cc. 0.5 % Sulfuric Acid. Pressure: 10 Atm.

Time in Minutes	Yield of Sugar in % of the Cellulose
15	20.1
37	37.3
45	38.2
60	39.0
75	40.0
90	42.7
120	35.0-40.9

Simonsen's results have been checked and confirmed by other investigators (276). The yield of sugar is, as J. Neuman and H. Ost (277, 278) in particular have emphasized, dependent not alone on the rapidity with which sugar is formed from the cellulose, but also on the speed of the decomposition of the sugar which has been formed. The following table summarizes the results of Neuman's investigations. One g. of glucose was heated for $1\frac{1}{2}$ hour at the following temperatures with 25 cc. of the given concentrations of sulfuric acid.

% H ₂ SO ₄	% Glucose Remaining Unreacted at			
	150° C	160° C	175° C	185° C
0.1	100.0	94.4	94.2	88.8
0.5	96.1	92.7	91.6	50.0
1.0	94.4	83.3	86.6	33.3
1.5	88.8	80.5	55.5	31.1
2.0	87.7	75.0	37.2	5.5
2.5	86.6	72.2	33.3	5.0
3.0	83.3	71.0	25.0	2.7
5.0	80.5	38.8	5.5	0.0

If the residues from the acid treatment of cellulose are treated with fresh acid under the same conditions, the yield of sugar decreases markedly (277); A. Wohl and K. Blumrich (279) attribute this fact to the formation of insoluble reversion products (dextrins) in the solid phase. These authors also believe that hydrolysis with hot, dilute acid yields not only simple glucose residues, but also carbohydrates of higher molecular weight, which can undergo further hydrolysis.

These findings are not in agreement with the recent investigations of E. Hägglund (280), who obtained the following average values from numerous experiments:

Saccharification of So-Called "Sulfite Fodder Pulp" (Practically Pure Cellulose + 1 % of Lignin) for 90 Minutes at 185° C. Ratio of Dilute Acid to Cellulose, 10 : 1.

Step of Hydrolysis	Yield of Sugar in % of Cellulose Initially Present in Each Step
A. With 0.3 % Sulfuric Acid	
1	32
2	33
B. With 0.5 % Sulfurous Acid	
1	35
2	40

According to these data, and in contrast to the ideas of Simonsen and Wohl, reversion does not occur before the saccharification is at least 50-60 % complete. The same result is obtained from the experiments of H. Lüers (281) and H. Scholler (282) on the kinetics of the saccharification of cellulose with dilute acids. These workers used a cellulose dextrin as their starting material, and found that it was quantitatively degraded to glucose under the conditions which they employed. The reaction velocity corresponded to a unimolecular reaction. The sugar formed underwent a decomposition, which also proceeded monomolecularly; no equilibrium occurred, therefore.

If x represents the quantity of sugar formed at time t , and a , the total amount of sugar which could be formed, then

$$\frac{dx}{dt} = k(a - x).$$

And if y represents the quantity of sugar decomposed in time t , and b , the original amount of sugar:

$$\frac{dy}{dt} = k_1(b - y).$$

Since the two processes proceed simultaneously, the actual amount of sugar present, z , is given by

$$z = x - y.$$

Hence

$$\frac{dy}{dt} = k_1(x - y).$$

From these differential equations one obtains the result that

$$z = \frac{ak}{k_1 - k} (e^{-kt} - e^{-k_1t}).$$

The velocity constants k and k_1 are proportional to the hydrogen ion concentration. If γ and γ_1 are the velocity constants for the formation and decomposition of sugar when the hydrogen ion concentration is 1, and the actual hydrogen ion concentration during the experiment is denoted by h , then we have

$$k = h\gamma \text{ and } k_1 = h\gamma_1$$

whence we derive

$$z = \frac{a\gamma}{\gamma_1 - \gamma} (e^{-\gamma ht} - e^{-\gamma_1 ht}).$$

At a temperature of 170° C. γ and γ_1 were found to be 6.49 and 7.86, respectively. The dependence of the velocity constants on the temperature is shown in Fig. 46.

According to these curves, the values of γ and γ_1 at 160° C. are 3.25 and 3.93; the temperature coefficient is therefore 2. Fig. 47 shows how the curves would run, both at 170° C. and at 160° C., if no decomposition of the sugar occurred (curves X), and also the actual course of the curves when the sugar is more or less decomposed (curves XIV). H. Lüers points out quite rightly that no "equilibrium state" occurs. The yield of sugar rises rapidly at first, reaches a flat maximum, and then declines slowly.

The kinetics of cellulose hydrolysis and glucose decomposition in 0.1-1.6 % sulfuric acid and at temperatures between 170 and 190° C have recently been studied by J. F. Saeman (283).

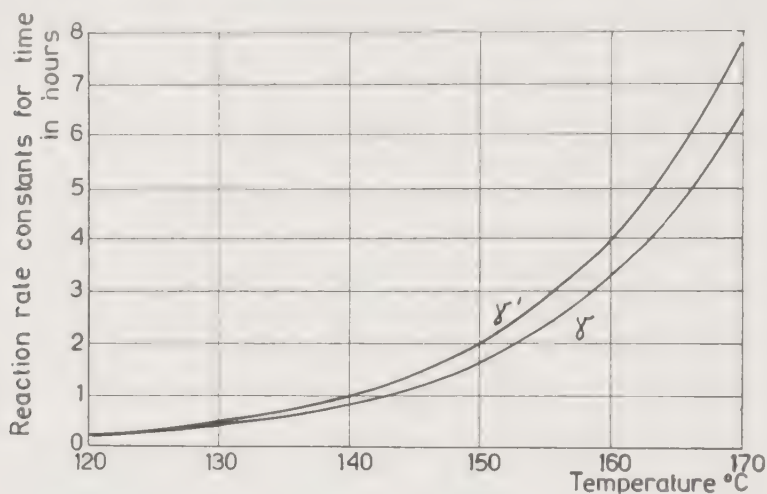


Fig. 46. Temperature dependence of the reaction rate constants (γ and γ') for the formation and decomposition of sugar.

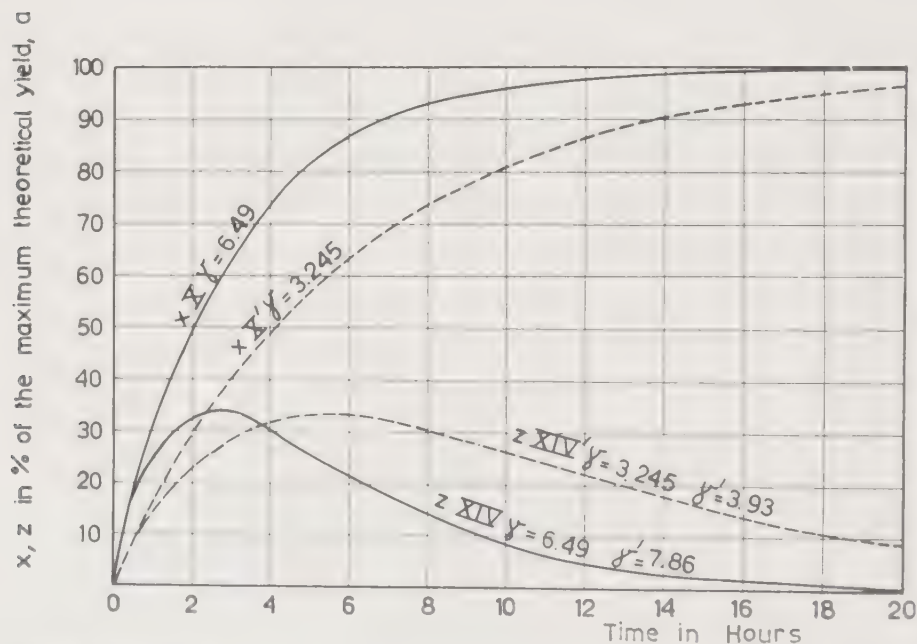


Fig. 47. Sugar present, in per cent of the maximum theoretical yield, at 160° C (---) and 170° C (—). X, theoretical curve, assuming no decomposition. XIV, actual curve.

The significance of these results in the practical saccharification of wood with hot, dilute mineral acids will be discussed in more detail in another place (Chapter IV).

The experiments of Lüers and Scholler are of theoretical interest in that they prove that the saccharification of cellulose with dilute acids appears to proceed according to simpler laws than the degradation with strong sulfuric acid (281); this point has already been mentioned above.

K. Freudenberg (285) believed that he had explained this matter when he assumed that the degradation of cellulose in a heterogeneous system is comparable to the solution of a powdered metal in acid; this process, like the heterogeneous saccharification of cellulose is "approximately" unimolecular. The speed of the heterogeneous saccharification was assumed to be governed not by the rate of saccharification of the fragments which had been brought into solution, but by the rate of solution, which is much less. The slowness of solution was attributed to the fact that the acid does not penetrate the cellulose fibrils rapidly and that therefore only the peripheral cellulose chains can be dissolved.

Very complicated relationships sometimes arise, however. O. Ant-Wuorinen (286) found, for example, that considerably greater quantities of sugar were formed at the beginning of the process than later, if cotton cellulose, viscose fibers, or cellulose precipitated from sulfuric acid were hydrolyzed with boiling 5 *N* sulfuric acid, or with 5 *N* sulfuric acid at the temperature of a water-bath. C. G. Schwalbe (287) had also found much earlier that the copper numbers of various celluloses were very different after 15 minutes of boiling with dilute sulfuric acid. The copper number of artificial silks rose by 11.5, for example, while that of mercerized cotton increased by only 3.7. One would expect that the glucose formation would increase with the time, because of the splitting of the chains. Ant-Wuorinen thinks that only the non-ordered portions of the cellulose are readily attacked, while the micellar regions are better protected against the action of the acid. The degradation of cellulose chains during the formation of hydrocellulose can, of course, be explained in the same way.

Investigations made by A. Bujewskoi (288) seem to indicate that the hydrolysis of cellulose and its degradation products and derivatives also depends on the extent to which the glucose linkages are accessible to the reagent (285).

R. F. Nickerson (289) extended the investigations of hydrolysis to many other materials (Fig. 48). The hydrolysis was carried out in 9% hydrochloric acid. When ferric chloride is present, the degradation of cellulose can under suitable conditions be followed quite well by the evolution of carbon dioxide from the glucose which is formed (290). Nickerson also concludes from his results that the crystalline regions are difficultly attacked, while the amorphous regions are easily split (cf. also p. 61).

As R. E. Reeves, V. M. Schwartz and J. E. Giddens (291) have shown,

treatment of cellulose with 0.5 per cent solutions of hydrogen chloride in methyl or ethyl alcohol results in an alcoholic splitting of the 1,4-glycosidic bonds. A trans-acetalisation occurs and the reaction products, containing glycosidic alkoxy groups, do not reduce Fehling's solution and are, in contrast to the hydrolytic cleavage products, stable to warm alkali.

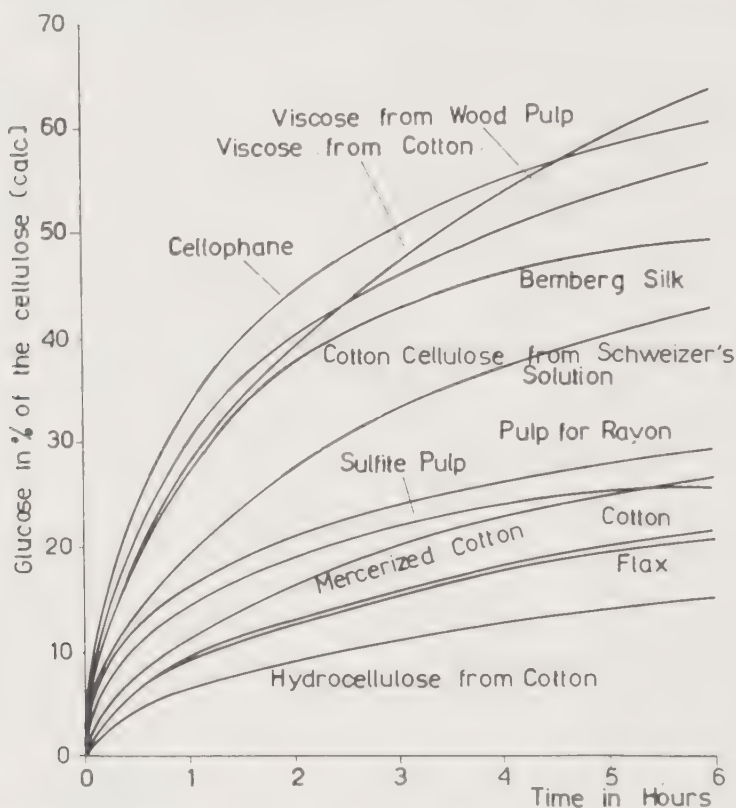


Fig. 48. Hydrolytic degradation of natural and regenerated celluloses by boiling with 2.4 N hydrochloric acid to which ferric chloride (0.6 mol/liter) has been added.

The changes wrought in cellulose by the action of *concentrated hydrochloric acid* have been studied by many workers. R. Willstätter and L. Zechmeister (292) investigated the optical properties of the cellulose solution at various times, and found that the solution is optically inactive at the beginning, but that the optical rotation increases more or less rapidly, depending on the concentration of the acid, and after 24-48 hours attains a maximum which corresponds to the rotation of glucose. The increase in rotation does not proceed uniformly; the curve shows a sharp angle, indicating the formation of an intermediate compound. The rotation indicates the presence of more sugar than corresponds to the reductive power of the solution; this also points to the presence of intermediate compounds. Toward the end of the reaction the intermediate

compound is not formed as rapidly as it is decomposed into glucose. It is noteworthy that no formation of isomaltose occurs during this process; this is due to the extreme dilution of the solution. The changes in the optical rotation were later investigated by E. Heuser and E. Boedeker, with the following results (293):

1 g. Cotton Cellulose in 100 cc. 41.4 % Hydrochloric Acid, 20° C

Time in Hours	% Glucose, Determined by Reducing Value	% Glucose, Determined Polarimetrically
15	90.65	92.30
16	94.66	96.15
16 ¹ / ₄	96.33	96.15
16 ¹ / ₂	97.29	100.00
16 ³ / ₄	94.78	96.15
17	90.59	92.30
18	77.26	80.77
20	56.20	57.70

Theory requires a yield of 111.1 % of glucose. These results do not agree with those of Willstätter and Zechmeister in that a considerable recession in the rotation is observed. This is caused by a reversion of the glucose which goes into solution at first. Concentrated solutions of cellulose yield still greater quantities of isomaltose and other reversion products, which can be more or less quantitatively hydrolyzed to glucose by diluting and heating the solution (294).

The reversion of glucose has been studied in detail by H. Frahm (295), who also found that the extent of reversion increases with the concentration of the solution. When cellulose was hydrolyzed with concentrated hydrochloric acid it was found that the degradation product corresponded to the reversion product, both in optical rotation and in reducing power. The degradation of cellulose goes then, first to glucose, which subsequently undergoes reversion. After 25 hours equilibrium is established; the reducing value at equilibrium corresponds to 41-43 % of glucose.

Reversion products are also formed in hot, 0.25-0.5 per cent hydrochloric acid under pressure of about 3 atm., conditions like those used in technical procedures for the hydrolysis of starch. These reversion products consists chiefly of isomaltose (6- α -glucosidoglucose); some gentiobiose is also formed [about 5 % of the total amount of glucose (296)].

H. Ost established the important fact that the saccharification is incomplete in concentrated solutions of cellulose in hydrochloric acid of specific gravity 1.204. The velocity of the reaction is also much less. We shall return to this question in another connection (cf. Chapter IV).

E. C. Sherrard and A. W. Froehle (297) have also investigated the degradation of cellulose in strong hydrochloric acid. They compared

cellulose from birch, Douglas fir, and white pine with that from cotton, and found not one, but two breaks in the curve. K. Hess and H. Friese (298) followed with the polarimeter the hydrolysis of linters in 40 % hydrochloric acid in the presence of 40 % of zinc chloride; they confirmed the fact that a definite break in the curve occurs, and concluded from this that an intermediate product is formed.

M. L. Wolfrom and L. W. Georges (299) likewise followed the degradation of cellulose in concentrated hydrochloric acid by polarimetric measurements, and concluded from the rate of increase in the rotation that the rate constants of the monomolecular reaction increase slightly. They did not find breaks in the curve; this is in agreement with the results of H. Hibbert and E. G. V. Percival (300), who studied the increase in rotation of cellulose in zinc chloride-hydrochloric acid solutions. Wolfrom and Georges also followed the reaction by adding ethyl mercaptan, which in the hydrochloric acid solution reacts with the aldehyde groups of the intermediate products.

M. L. Wolfrom (301) and his co-workers later investigated the degradation of trimethylcellulose by fuming hydrochloric acid, in the presence of ethyl mercaptan. The trimethylcellulose was prepared from acetone-soluble acetylcellulose, and had an average degree of polymerization of 150. Monomolecular reaction rate constants were found for the process of splitting to a molecular weight one-third that of the original material.

It is possible to obtain a 100 % yield of glucose on hydrolysis with concentrated acid, if special experimental conditions are maintained.

A. Kiesel and N. Semiganowski (302) suggest that a quantity of 80 % sulfuric acid equal to 7-10 times the amount of cellulose be used for the sulfolysis, and that the solution be diluted before the cooking by adding 15 cc. of water per cubic centimeter of sulfuric acid. They carry out the cooking under reflux on a water bath, and claim that they are thus able to achieve a quantitative saccharification.

E. Hägglund and L. C. Bratt (303) have obtained quantitative saccharification with 72 % sulfuric acid. In their process 5 g. of air-dry material was treated with 45 cc. of 72 % sulfuric acid at room temperature. The mass was stirred in a beaker with a glass rod to insure complete permeation of the acid into the mass, and the beaker was then evacuated in a desiccator two or three times to remove the dissolved air. After four hours the reaction mixture was dilute with 95 cc. of water, and allowed to stand six hours more at room temperature. The solution was then transferred to a 2-liter flask, diluted with 1,500 cc. of water, and refluxed for six hours.

J. F. Saeman, Z. L. Bubl, and E. E. Harris (304) obtained a quantitative saccharification of cellulose under quite similar conditions.

H. H. Schlubach, H. Elsner, and V. Prochownick (305) report that cellulose is disintegrated smoothly when it is treated with *dry hydrogen chloride* under pressure at 20° C for 10 hours. Glucose anhydride, as well as the anhydrides of di- and trisaccharides were formed in quantitative yields.

K. Hess and M. Ulmann (306) have measured the speed of this reaction and found that, except for the last part of the reaction, the equation $\frac{dx}{dt} = K(a-x) \frac{1}{l}$ holds, where l is the path of diffusion for the hydrogen chloride from the surface of the fiber to the point of reaction, and $(a-x)$ is the amount of cellulose which remains unreacted at time t . The product obtained always contained chlorine, and had the composition $(C_6H_{10}O_5)_2 \cdot 3 HCl$. [Schlubach and Prochownick (307) found a lower chlorine content, corresponding to that of α -glucosyl chloride.] This substance is water-soluble. It is also formed within the fibers, even in the presence of water. Under some circumstances a reaction then follows which results in the formation of another cellulose-HCl compound which is not attacked by liquid HCl, but which probably is attacked by aqueous HCl. It has not yet been possible to decide whether reversion products of the glucose are formed under these conditions.

In this connection it is worthy of notice that H. H. Schlubach and E. Lührs (308) treated glucose with dry hydrogen chloride at its saturation pressure (43 atm.) and obtained a *chlorine-free* product containing 60 % of polyglucosan, 30 % of trisaccharide, and 10 % of unchanged glucose. The reversion evidently increases sharply with increasing hydrogen chloride concentration.

K. Hess, F. Stricker and R. Rutkowski (309) found that under similar conditions a labile chlorine-containing intermediate of the composition $C_6H_{12}O_6 \cdot HCl$ is formed. On treatment with methyl alcohol it yields methoxyl-containing low-molecular reversion products and therefore is believed to have the structure of a 1,1-dichlorohydrin.

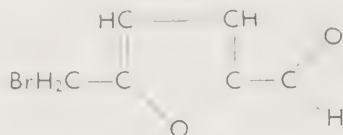
B. Helferich and St. Böttger (310) and K. Fredenhagen and G. Cadenbach (311) found that *hydrofluoric acid* dissolved cellulose almost instantaneously, to give a clear and colorless solution. The oxygen bridges of the cellulose were split, and glucosyl fluoride was formed:



Glucosyl fluoride is converted to glucose and hydrogen fluoride in the presence of small quantities of water. Attempts to precipitate glucose out

of solutions in hydrogen fluoride or to evaporate them to dryness result in the formation of polyglucosans. These are converted into glucose by cooking with dilute acids.

Both cellulose and starch form α -bromomethylfurfural in about one-third of the theoretical yield when they are treated with *hydrogen bromide* in certain nonaqueous solvents (such as chloroform):



Cellulose exhibits a behavior similar to that of starch, the β -glucosides, or β -glucose, in that on vacuum distillation it gives rise to a glucose anhydride, levoglucosan (312). The levoglucosan is formed in considerable quantities, which may run as high as 37 % (313).

5. Cellulose and Alkalies. So far as the behavior of cellulose toward *dilute* alkalies at ordinary temperatures is concerned, it may be stated that cellulose exhibits a greater resistance to the action of alkalies than to that of mineral acids.

When cellulose is treated with hot, dilute alkalies, it gradually dissolves more or less completely, with the formation of decomposition products which have not been further investigated. The following early experiments of H. Tauss (314) may be mentioned.

Ten grams of cellulose were first cooked at atmospheric pressure with 500 cc. of sodium hydroxide. It then appeared that a sort of reversion occurred in the solid phase, for when the cooking was repeated the quantity of material dissolved decreased, and a third cooking gave a further decrease in the amount of material dissolved. Part of the dissolved material could be precipitated from the solution with alcohol. No study was made of the nature of the degradation products.

Concentration of Sodium Hydroxide, in %	Duration of Action (Hours)	Amount of Cellulose Dissolved	
		g.	%
4	3	—	12.07
8	3	1.699	16.99
8	6	0.487	21.86
8	9	0.093	22.79

F. Hoppe-Seyler (315) also studied the decomposition of cellulose with alkali and water, at temperatures of 200-240° C. He found that the degradation products contained small amounts of formic, acetic, and higher-boiling acids, as well as some pyrocatechol and protocatechuic acid.

It is probable that the latter two substances are not derived from the cellulose, but from impurities such as lignin, which are present in the starting material (filter paper).

F. Fischer and H. Schrader (316) have also heated cellulose (filter paper) with alkali. Their results are given in the following table:

30 g. Cellulose+50 cc. Alkali. Time: 3 Hours

Alkali	Temp. °C.	Gas Evolv- ed cc.	CO ₂ in Gas cc.	Residue, or Mate- rial Pre- cipitated Out g.	Acids from the Alkaline Solution Precipi- tated on Acidifica- tion g.	Volatilized with Steam		Ex- tracted with Ether g.
						Total cc. N	Formic cc. N	
KOH 4.1 N.	200	5	—	10.8	0.74, Not volatile insol. in water	Not detd.	49.4	1.6
KOH 4.1 N.	300	1,245	331	3.0+1.3 g. oil	1.0	20.6	Much	1.0
NaOH 5 N.	300	1,810	1,412	0.6+1.4 g. oil	1.1	Not detd.	38.0	3.3

Even dilute solutions of the alkaline earth bases dissolve a part of native cellulose. C. G. Schwalbe and E. Becker (317) have proposed the use of baryta water instead of mercerizing liquor (17-18 % NaOH) for determining the amount of the cellulose in various preparations which is capable of resisting the action of alkali. B. Tollens, I. Sack, and J. Muruchow (318) had discovered much earlier that lime water dissolves the degradation products of cellulose, while the cellulose which has not been attacked remains undissolved. The yield of cellulose resistant to baryta is not always the same as the α -cellulose content of the preparation, which is determined with 17-18 % sodium hydroxide (mercerizing liquor).

The behavior of cellulose on *fusion* with alkali is of interest in this connection. Systematic investigations of this point were carried out by E. Heuser and F. Herrmann (319), who obtained no aromatic substances, but 90-91.4 % of oxalic acid, 21-22 % of acetic acid, and 1.6-2 % of formic acid. Oxalic acid is not produced by oxidation, but perhaps by an "alkali hydrolysis."

6. The Degradation of Cellulose by Heating in the Presence of Water. The behavior of cellulose when it is *heated with water alone* is worthy of mention. Such experiments were probably first carried out by F. Bergius and H. Specht (320). They report the following results:

Quantity of Dry Material Used g.	Temp. °C.	Time hrs.	Gas Evolved cc.	Elementary Analysis of the Residual Charcoal			
				C	O	H	Ash
13	250	8	940	74.73	20.34	4.87	0.26
13	340	8	—	82.88	11.68	5.14	—
13	310	64	1,415	83.49	10.85	5.36	0.3

The gases consisted of 98.6-99.3 % of carbon dioxide, small amounts (0.2-0.6 %) of unsaturated hydrocarbons, methane (0.6 %), and hydrogen (0.2-0.5 %).

On the basis of the last experiment, Bergius formulates the decomposition as follows:



It is noteworthy that three molecules of water are given off for every $\text{C}_6\text{H}_{10}\text{O}_5$ residue; this fact may be connected with the occurrence of three hydroxyl groups in cellulose. According to Bergius the decomposition of cellulose is a spontaneous reaction at ordinary temperatures, and cellulose is therefore extremely unstable (thermodynamically) at room temperature.

Bergius' experiments have been checked by H. Tropsch and A. v. Philippovich (321) in Franz Fischer's institute. The results obtained were quite different from Bergius', in that besides the water-insoluble charcoal, large quantities of *water-soluble* degradation products and volatile compounds were obtained. Hence Bergius' theoretical calculations with reference to the coalification process must be regarded as unjustified.

F. Bergius and P. Erasmus (322) later studied this problem more thoroughly. The first stage of the formation of coal, which takes place in nature during the formation of peat, occurs in a few hours at 250°C , and corresponds to the equation:



This reaction causes the carbon content to rise from 44.5 % to 62.5 %. The product formed is not soluble in alkali, as long as oxygen is excluded, but on oxidation it takes up two atoms of oxygen with extreme rapidity, so that the coalification, including oxidation, proceeds according to the equation:



Humic acids are formed, which were called by Odén (cf. Ch. XII, ref. 1) "marsh humic acid", $\text{C}_{12}\text{H}_8\text{O}_6$, and "hymatomelanolic acid", $\text{C}_{12}\text{H}_{10}\text{O}_5$.

The compound $\text{C}_{12}\text{H}_{10}\text{O}_5$ is degraded, with loss of carbon dioxide, by long-continued heating to high temperatures. There is eventually formed an "end charcoal" containing 84.2-84.7 % of C, and 4.5-4.9 % of H. It is remarkable that the end charcoal has the same composition even when it is derived from the most varied sources, such as straw and lignin, for example. The end charcoal is not uniform, but consists chiefly (about 70 %) of a substance with the formula $\text{C}_{20}\text{H}_{20}\text{O}_2$, which is soluble in a

mixture of benzene and alcohol, and of an insoluble substance corresponding to the formula $(C_{10}H_6O)_x$. Bergius has called the first substance α -charcoal, and the second, β -charcoal.

Under the conditions used in the manufacture of fiber pulp according to the Masonite process, a smaller part of the wood polyoses as well as some lignin is dissolved (322 a). The extracted material has the following composition: 70 % wood sugar, 10 % lignin and 20 % resins. The sugar is polymer and consists of about 65 % hexosan and 35 % pentosan.

Similar hydrolytic reactions also take place in the Asplund process (322 b), in which wood chips are disintegrated to fibers in the presence of steam at 160-180° C.

S. I. Aronovsky and R. A. Gortner (323) treated aspen sawdust with water at 170 or 186° C, and found that the weight of the sawdust decreased by 25-40 %. They found that a part of the lignin had been rendered soluble in alcohol after the heating under pressure. According to C. G. Schwalbe (324) the material which dissolves in water consists of sugars and of wood gum (xylan), with the possible addition of split-products from the lignin or of humus. The presence of acetic and formic acids was also proved at an early date, along with that of methyl alcohol and furfural. W. H. Dore (325) was the first to establish the fact that the acetyl group was carried by the xylan, and not by the lignin, as had long been thought.

Heating of wood with water under pressure at 130-150° C for two hours causes 12-14 % of carbohydrates to dissolve out of spruce, and about 26 % out of beech, according to W. Overbeck and H. F. Müller (326). These authors are of the opinion that the acetic and formic acids cause a hydrolysis to occur. The carbohydrates dissolved are polymeric. Part of the lignin in the residue can be dissolved in alcohol, and a second part is soluble in dilute alkali at low temperatures. A part of the lignin is made more difficultly soluble in bisulfite by the heating with water. It is possible to dissolve out small amounts of a labile lignin-carbohydrate compound by brief treatment with water under pressure, but it is not possible to cause larger quantities of carbohydrate to go into solution without damaging the lignin. This can be explained on the assumption that the lignin is chemically linked to the carbohydrate. When the linkage is broken, the lignin is converted to an easily-soluble form. On the other hand, condensations can now occur at the linkage points, causing the lignin to increase in molecular weight, and become insoluble in bisulfite solutions.

F. Schütz (327) studied the same question, and came to conclusions which were the same in some respects, but different in others. He heated

beech wood with water at 100-105° C, and observed that the formation of acetic acid increased with time, reaching a maximum after three to four days. A total of 4.5-5.2 % of acetic acid was found, whereas the amount of formic acid was very small. Schütz was struck by the fact that considerable quantities of carbon dioxide were formed. He found that the carbon dioxide was formed from wood in the presence of water even at room temperature. If the acetic acid produced during pressure heating was neutralized, carbon dioxide still appeared. From these results he concluded that an acid reaction during the hydrolysis of wood was not necessary for the solution of carbohydrate, as Overbeck and Müller had thought. The quantities of products formed are always larger than would be expected on the basis of the loss in weight of the residue. In the case of beech wood, the gain in weight amounts to about 4.3 %; the water must therefore play a fairly important part in the reaction.

The methoxyl content of the materials going into solution is very high, running from 4.3 to 10.1 %; the carbon content is 45-49.8 %, which is higher than that of cellulose. The elementary composition of the wood is scarcely affected by the heating under pressure. The substances dissolved out were presumed from their composition and chemical behavior to consist of glucosides, one of whose components is an aromatic phenol containing methoxyl groups, and the other component of which is a carbohydrate.

F. Schütz and P. Sarten (328) have continued these investigations. When wood is treated with water at elevated temperatures, considerable quantities of material go into solution. The extracts have approximately the same composition as the wood itself, for the analyses of the residues are not much different from those of the starting materials. The materials dissolved out apparently yield lignin on treatment with acids, or even with warm water. Consequently, the authors accepted the idea of Hilpert (cf. p. 181), that lignin is not pre-formed in the wood, but that it is formed from unknown, sugar-like substances. They believed that this viewpoint is supported by the fact that they were unable to isolate normal azo dyes by the action of diazotized sulfanilic acid, for example, on wood, as would be expected if the lignin were present in the wood in the form of a phenol (cf. also p. 182).

7. The Degradation of Cellulose by Dry Distillation. A. Pietet and J. Sarasin (329) have found that the distillation of cellulose *in vacuo* gives levoglucosan in approximately 30 % yield. About 10 % of residue is also formed, along with 32 % of watery distillate, and 13 % of gases.

Many studies have been made of the dry distillation of cellulose at atmospheric pressure. Some rather old experiments of J. C. Chorley and W. Ramsay (330), who distilled cotton at a maximum temperature of 325° C, gave the following results:

	I %	II %	III %
Charcoal.....	34.33	34.44	33.00
Distillate.....	43.32	51.11	46.00
CO ₂	5.22	7.77	11.00
Other gases....	17.13	6.68	10.00
	100.00	100.00	100.00

The distillates contained, besides water, the following substances in the quantities shown below (calculated on the basis of the cellulose):

	I %	II %	III %
Tar.....	9.70	13.33	12.00
Acetic acid.....	1.75	2.11	1.31
Methyl alcohol..	3.94	10.24	7.07

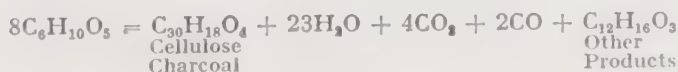
In connection with these results it should be remarked that the presence of methyl alcohol in the distillate was not confirmed by later investigations. The methyl alcohol formed during the distillation of wood is derived from the lignin, and not from the cellulose, according to the view of P. Klason in particular.

P. Klason, G. v. Heidenstam, and E. Norlin (331) have carried out dry distillations of various celluloses. The highest temperature attained was about 400° C; a temperature of 300° C was reached after 1-2 hours. Each experiment consumed about 12 or 13 hours.

The results of these experiments are summarized in the following table:

Product	% Yield from the Following Kinds of Cellulose					Yield Calculated
	Cotton	Pine	Spruce	Birch	Beech	
Charcoal.....	38.8	36.9	34.8	33.39	32.91	34.0
Water.....	34.5	34.2	30.0	29.35	31.88	32.0
Carbon dioxide.....	10.4	12.8	11.9	11.14	11.96	13.6
Carbon monoxide.....	4.2	3.4	3.9	3.49	3.80	4.3
Other products.....	12.26	12.67	18.2	22.23	18.52	16.0

According to Klason and his co-workers, the chemical reaction involved in the dry distillation of cellulose may be expressed by the following equation:



The elementary compositions of the cellulose charcoals were as follows:

Type of Cellulose	% C	% H	Caloric Value (Cal.)
Cotton.....	81.79	3.89	7,550
Pine.....	81.69	3.64	7,590
Spruce.....	81.32	4.23	7,750
Birch.....	83.7	4.30	7,980
Beech.....	83.1	4.1	7,840

The composition of the gases and of the watery distillates was also determined, with the following results:

Product	Percentage by Weight				
	Cotton	Pine	Spruce	Birch	Beech
Gases CO ₂	10.35	12.83	11.94	11.14	11.96
C ₂ H ₄	0.17	0.21	0.19	0.41	0.25
CO.....	4.15	3.40	3.92	3.49	3.80
CH ₄	0.27	0.27	0.22	0.47	0.39
Methyl alcohol.....	—	trace	0.07	—	0.19
Acetone.....	0.07	0.08	0.13	0.15	0.26
Acetic acid.....	1.39	2.18	2.79	3.89	3.50
Tar.....	4.18	4.85	6.28	9.58	5.23
Organic substances of unknown composition.....	5.14	4.22	8.50	7.72	8.67
Water.....	34.52	34.17	29.99	29.35	31.88
Loss.....	0.94	0.86	1.11	0.40	0.93

In connection with these figures it should be observed that the differences in behavior of the various kinds of cellulose are due to the fact that the wood celluloses are not pure. They were made by disintegration of the woods with bisulfite liquors, and the products thus obtained contain varying quantities of hemicellulose, whose chief constituent is pentosan. Hence, if celluloses from birch and beech yield more acetic acid than those from cotton and softwoods, this may be due to the greater content of pentosan. The fact that practically no methyl alcohol is produced supports the view of P. Klason, mentioned above, to the effect that methyl alcohol is formed chiefly from the lignin of the wood.

W. Wislicenus and G. Büttner (332) also carried out dry distillations of cellulose (filter paper) under various conditions; by using a higher temperature they were able to carry the decomposition farther than Klason had. No methyl alcohol was produced in this case, either.

The experiments of E. Erdmann and C. Schaefer (333), who likewise distilled filter paper, are also worth mentioning. The presence of the following substances in the watery distillate was established by qualitative tests: formaldehyde, furfural, maltol (in very small quantities), hydroxymethylfurfural, and γ -valerolactone.

The thermal decomposition of cellulose has been studied very thoroughly by Franz Fischer and his co-workers. F. Fischer and W. Schneider (334) obtained the following results:

	%
Coke.....	26.3
Water distillate.....	45.7
Tar.....	6.1
Gases.....	21.9

Distillation in an aluminum retort at temperatures varying between 270 and 500° C gave considerably higher yields of tar "primary tar" (335). The results of these experiments are summarized in the following table.

Weight of Starting Material g.	Water %	Primary Tar (Distillate Water) %	Semicoke %	Gas, Cal- culated as Difference %	In Primary Tar	
					Neutral Fraction %	Acid Fraction %
20	32.0	24.2	23.8	20.0	—	—
27.3	34.8	21.2	26.6	17.4	6.6	2.0, Sol. in soda, 1.7, Sol. in caustic alkali

The reason for the remarkably high yield of tar in comparison with the previous results (3.3-7.1 %) is according to Fischer and Schrader (who carried out the experiments summarized in the above table), that superheating is completely avoided by the use of an aluminum retort.

If the material is soaked in caustic soda before the distillation, the yield of tar is increased. F. Fischer and H. Niggemann (336) used 5 N sodium hydroxide, and found that the yield of tar increased from 5.5 % to 15 %.

F. Fischer and W. Schneider (334) showed that when cellulose is heated under pressure to 250-260° C with benzene it decomposed without any evolution of gas, and with the formation of products which are taken up by the benzene.

Damp cellulose gives higher yields than does dry material, as the following figures show:

Water-free cellulose, twice heated under pressure.....	2.0 % extract
Cellulose containing 5 % water, twice pressure-heated.....	6.4 "
Cellulose soaked in water.....	12.5 "

8. The Enzymatic Degradation of Cellulose.¹ The enzymatic degradation of cellulose is caused in nature primarily by the action of fungi, bacteria (including actinomycetales) and protozoa. The enzyme which splits cellu-

¹ This section has been most kindly prepared by Dr L. Enebo, Division of Microbiology, Royal Institute of Technology, Stockholm.

lose, cellulase, is found only in certain lower animals, like teredos and snails, e.g., *Helix pomatia*. The higher animals, probably including the insects, are not provided with cellulase, and the cellulose degradation which occurs in the metabolism of herbivorous animals is a symbiotic phenomenon caused by cellulose-splitting microorganisms (bacteria and protozoa) in the intestinal flora.

The discovery of the bacterial degradation of cellulose is usually attributed to E. Mitscherlich (337), who reported in 1850 that he had observed that the cell walls of pieces of potato immersed in water were fermented, thus releasing the starch granules. This phenomenon must now be regarded as an example of pectin-fermentation; it can easily be demonstrated by inoculating raw potatoes with *Clostridium felsineum*, which does not ferment cellulose (338). The true fermentation of cellulose (filter paper) was demonstrated in 1875 by Popoff (337). Fundamental researches in this field were carried out by W. Omelianski (337) around the turn of the century. Omelianski, who worked with elective cultures of mesophilic, anaerobic, spore-forming cellulose bacteria (temperature optimum 37°C), thought he had discovered two strains, both of which fermented cellulose to give lower fatty acids, carbon dioxide, and hydrogen, but which differed in that one also formed methane. P. Clausen (339) later showed that the formation of methane is a secondary process, brought about by special methane bacteria. It is now quite certain that the cellulose bacteria, the mesophilic as well as the thermophilic, form no methane.

The first reports on *thermophilic* cellulose fermentation (temperature optimum circ. 60°C) were published in 1889 by A. Macfadyen and F. R. Blaxall (340). Like the corresponding mesophilic process, the thermophilic degradation of cellulose is also caused by anaerobic spore-forming organisms, which belong to the *Clostridium* group. The isolation of the thermophilic organisms was, however, so difficult, that it was uncertain whether or not it had been accomplished until very recently [cf. L. Enebo (341) and R. M. McBee (341 a)].

The study of the *anaerobic* decomposition of cellulose was greatly hampered by the difficulty of isolating the bacteria. They appear to have a great tendency toward symbiosis with varieties which do not degrade cellulose. The function of the symbiotic bacteria has been explained by saying that they lower the redox potential of the medium to a value suitable for the growth of the cellulose bacteria, and provide the latter with certain essential nutritional factors. The first function can easily be dispensed with by various artificial means, but our knowledge of the nutritional requirements of the various *Clostridia* is still very incomplete.

and it has not yet been possible to compound vitamins, amino acids, and natural extracts into a substrate in which the thermophilic cellulose bacteria develop in a normal fashion, and degrade cellulose vigorously, as they do in symbiotic cultures. The circumstances are somewhat simpler in the case of the mesophilic types.

As a practical matter, one must therefore regard the thermophilic fermentation of cellulose as an anaerobic, symbiotic process caused by a mixture of cellulose bacteria with other bacteria. Some of the latter are important, but others are not necessary, and may be removed from the culture without interfering with the course or velocity of the process.

Recently, L. Enebo (341) succeeded in finding a simple agar plate method for the isolation of thermophilic cellulose fermenting bacteria in pure culture. The substrate contains cellulose dextrin and potatoextract as well as 0.03 % thioglycolic acid¹. As it could be expected, the cellulose breakdown in the pure cultures was incomplete, compared with the mixed cultures. When fermentation ceased, the medium contained considerable amounts of glucose and cellobiose. This proves the fact that a pure culture really had been obtained, since otherwise the symbionts should have utilized these sugars. The cellulose fermenters do not form butyric acid, in contrast to the non-cellulose-fermenting symbionts. The table below shows the result of cellulose decomposition by the cellulose fermenter both in pure culture and together with one or two glucose fermenting symbionts. The last-mentioned combination is the same as that used in the experiments summarized in the table on page 113.

Grams of Fermentation Products per 100 g. Decomposed Cellulose when Fermented by Different Cultures²

Added cellulose: 10 g./liter medium

c = Pure culture of cellulose fermenting bacterium

s = Pure culture of butyric acid bacterium, fermenting glucose

III = Pure culture of lactic acid bacterium, fermenting glucose

Culture	c	c + s	c + s + III
Incubation time, days....	10	8	6
Cellulose fermented, %...	40.1	70.1	100.0
<i>Fermentation products:</i>			
(g./100 g. fermented cellulose or glucose)			
Ethanol.....	16.0	13.7	15.0
Formic acid.....	5.4	1.1	1.7
Acetic acid.....	19.1	42.2	29.0
Butyric acid.....	0.0	14.2	30.0
Lactic acid.....	43.1	9.6	4.8
Reducing substance, calculated as glucose.....	11.7	0.0	0.0

¹ Pure cultures were also obtained by R. M. McBee (341 a) by using the roll tube technique of Huugate.

² Succinic acid, which also is formed, is not determined in these experiments.

The aerobic cellulose bacteria belong chiefly to the genera *Cellulaccula*, *Cellvibrio*, *Cellulomonas*, *Cytophaga*, and *Sporocytophaga*. The numbers of species listed under these genera in Bergey's Manual are 3, 4, 18, 10, and 3, respectively. In addition, there are listed a large number of bacteria which attack cellulose, but whose descriptions in the original literature was not sufficiently detailed to enable them to be classified. It is also probable that there exist a number of additional cellulose bacteria which have hitherto been overlooked.

A. G. Norman (342) has emphasized that the use of purified cellulose (like filter paper) as a test for cellulose-splitting activity has caused those organisms which only attack cellulose in its native state to be overlooked. These organisms react first with the hemicellulose, after which the attack on the cellulose itself can begin.

The genus *Cytophaga* (which has recently been divided by R. Y. Stanier (343) into *Cytophaga* and *Sporocytophaga*) has received the most attention among the aerobic cellulose bacteria. A type of cellulose bacterium discovered in 1903 by G. van Iterson (344) was probably a member of this genus, but the fundamental work on *Cytophaga* was published in 1919 by H. B. Hutchinson and J. Clayton (345). These authors isolated a type which they designated as *Spirochaeta cytophaga*. S. Winogradsky (346) later proposed the genus name *Cytophaga*, and H. Krzemieniewska (347) showed that this genus was closely related to the *Myrobacteria*. Stanier's division is based upon the fact that *Sporocytophaga*, in contrast to *Cytophaga*, passes through a peculiar developmental cycle in which the cells change from rods to spherical structures (microcysts) and then back again to rods. In the modern nomenclature, *Spirochaeta cytophaga* is known as *Sporocytophaga myxococcoides*.

The *Cytophaga* bacteria, like the anaerobic cellulose bacteria, are to a certain extent specifically adapted to cellulose as a substrate, and do not grow on compounds which are usually good bacterial media, e.g. peptones, amino acids, sugars, salts of organic acids etc. According to older reports, reducing sugars in particular were supposed to inhibit growth, even in very low concentrations, but it was later shown, by G. Fåhræus (348) among others, that *Cytophaga* can grow in glucose solutions containing up to 0.5 % of glucose. Cellobiose and mannose are also utilized by these microorganisms.

A large number of fungi attack cellulose in various forms. Among the *Ascomycetes* one may mention varieties belonging to the genera *Aspergillus*, *Penicillium*, *Chaetomium*, *Ustilina*, and *Nylaria*. The *Fungi imperfecti* include cellulose-degrading forms, particularly in the genera *Candida*, *Trichoderma*, *Botrytis*, *Cladosporium*, *Alternaria*, and *Fusarium*. The

fungi which attack wood belong, with few exceptions, to the *Basidiomycetes*. Particularly important are *Armillaria*, *Collybia*, *Lentinus*, *Pholiota*, *Schizophyllum*, *Echinodontium*, *Hydnum*, *Daedalea*, *Fistulina*, *Fomes*, *Ganoderma*, *Lenzites*, *Merulius*, *Polyporus*, *Polystictus*, *Poria*, *Trametes*, *Coniophora*, *Hymenochaete*, *Peniophora*, and *Stereum*. Some of these organisms also attack lignin, and rotting wood therefore has different appearances, depending on the organism causing the decay. (Cf. Chapter XII.)

Although aerobic degradation of cellulose plays a greater role in nature and is hence of paramount importance, the anaerobic transformation of cellulose is of considerable interest from a practical standpoint. The anaerobic mesophilic fermentation of cellulose is one step in the biological purification of sewage. The organic acids and the alcohol produced by the cellulose fermentation, together with carbon dioxide, undergo an oxido-reduction through the agency of special methane bacteria, the carbon dioxide being reduced to methane, while the acids and alcohols are oxidized.

Intensive attempts have been made to use the thermophilic fermentation of cellulose for the production of organic acids and alcohol from worthless cellulose wastes. H. Langwell (349) has worked extensively in this field. However, the plants which were put into operation around 1930 were later abandoned as unprofitable. The acids, particularly acetic acid, which were formed in concentrations of not more than 2 %, were isolated by neutralization and evaporation of the fermented mash, and this process proved to be expensive. Enebo (350) has recently proposed recovering the acids by extraction, the fermentation being so regulated (by adjusting the pH) that the chief product is butyric acid.

The following table, due to L. Enebo (350), will illustrate the relative amounts of various products obtained in the thermophilic fermentation of cellulose at various pH's.

*Grams of Fermentation Products per g. Fermented Cellulose*¹

Buffer	MgCO ₃	CaCO ₃	SrCO ₃	BaCO ₃
pH, range.....	7.4-7.0	6.2-5.8	6.0-5.5	6.4-5.7
pH, average.....	7.1 (7.13)	5.9 (5.94)	5.7 (5.65)	6.0 (6.00)
Ethanol.....	0.126	0.009	0.015	0.069
Formic acid.....	0.134	0.003	0.000	0.006
Acetic acid.....	0.137	0.130	0.124	0.073
Butyric acid.....	0.000	0.367	0.298	0.190
Lactic acid.....	0.526	0.138	0.018	0.207
Total products	0.923	0.647	0.455	0.545

¹ Succinic acid not determined.

The experiments upon which the above table is based seemed to indicate that the thermophilic fermentation of cellulose took place between the pH limits of 5.5 and 8.5. Fahraeus (348) found exactly the same values for the aerobic degradation with *Cytophaga*.

As to the mechanism of the degradation of cellulose, it is generally assumed that the first reaction is a hydrolytic split by the enzymes cellulase and cellobiase to give soluble carbohydrates, specifically cellobiose and glucose. That this is true of the breakdown by anaerobic cellulose bacteria was demonstrated as early as 1912 by H. Pringsheim (351) who succeeded in inhibiting a part of the enzyme complex by adding iodoform to a culture of thermophilic bacteria while the degradation was going on. The end product of the partially inhibited enzyme complex was cellobiose, which was further split to glucose only to the extent that the inhibiting effect was decreased. A similar effect was obtained by decreasing the temperature of fermentation to 20° C; the end product was glucose in this case. As mentioned above, Enebo (341) has obtained glucose and cellobiose when using pure cultures.

Fahraeus (348) has found that the degradation by *Cytophaga* also begins with an hydrolysis. Since both anaerobic and aerobic cellulose bacteria are inhibited by large amounts of soluble carbohydrates, Norman (352) has raised the question as to the extent to which the hydrolysis really proceeds to cellobiose and glucose, before a further reaction sets in. Cellulose dextrans with 10-15 glucose residues are soluble in water and might possibly be able to diffuse into the cells.

To judge from its functional activity cellulase is certainly an ectoenzyme; for otherwise it would be impossible to explain the solution of cellulose fibers. A filtered solution of a cellulose bacteria culture, however, contains no cellulase. An attempt has been made to explain this on the basis that the cellulase is not secreted until the cells come in contact with the cellulose fiber. This viewpoint is supported by the fact that the cellulose bacteria are localized on the fibers, so that the nutrient medium as such is almost clear, when one has a pure culture of cellulose bacteria. A. I. Virtanen (353) has expressed the somewhat different opinion that the cellulase is attached to the cell wall, so that direct contact between the bacterial cell and the cellulose fiber is necessary for the action of the enzyme.

It is necessary to distinguish between an attack on purified cellulose and one on native cellulose. Certain substances present in native cellulosic materials afford some protection against the action of bacteria or fungi. Lignin protects against the action of bacteria, for example. On the other hand, native cellulose materials generally contain substances like hemi-

cellulose which are more easily attacked by microorganisms than is cellulose, itself. The "initial attack" is made upon these substances, and can then spread to the cellulose.

The structure of the cellulose-containing material is also important in determining the possibility of attack by microorganisms. A sheet of cellophane is, for example, more resistant to attack than is finely-divided cellulose. Virtanen and his co-workers (354) have shown that when wood cellulose is finely ground, the protective action of the lignin is partly removed, so that cellulose-fermenting bacteria are able to attack the ground material, whereas sawdust is completely resistant. (Cf. p. 303). According to F. R. Olson, W. H. Peterson, and E. C. Sherrard (355), wood cellulose (not finely ground) is fermentable provided that its lignin content does not exceed 1 %.

Very little is yet known about the mechanism of the further transformation of the hydrolytic degradation products of cellulose. In the case of the anaerobic cellulose bacteria which produce appreciable amounts of organic acids and alcohols, it may be supposed that the fermentation of the primary hydrolytic products proceeds in a manner similar to that with other bacteria, like the butyric acid bacteria, which are in many respects similar to the cellulose bacteria. Since most of the observations have been made with mixed cultures, or with cultures of doubtful purity, it is difficult to determine which reactions are due to the cellulose-fermenting bacteria, and which to the accompanying organisms. The end products of the fermentation seem to depend particularly upon the pH (see above). It has been known since 1936 that the yield of alcohol increases with increasing pH [M. K. Veldhuis, L. M. Christensen, and E. I. Fulmer (356)].

Virtanen (353, 357) has recently reported some observations from which he concluded that in thermophilic cellulose fermentation acetic acid is formed by a reduction of carbon dioxide with hydrogen:



In mesophilic cultures a reaction between methane and carbon dioxide seems to give acetic acid:

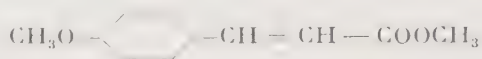


C. Neuberg and R. Cohn (358) have isolated acetaldehyde as an intermediate in the enzymatic degradation of cellulose.

According to F. F. Nord and J. C. Vitucci (359) the terminal product of the action of wood-destroying molds (*Merulius niveus*, *M. tremellosus*, *M. confluent* and *Fomes annosus*) is oxalic acid. The following pathway of degradation is postulated:

Cellulose \rightarrow Glucose \rightarrow Ethyl Alcohol \rightarrow Acetic Acid \rightarrow Oxalic Acid. Also in the formation of oxalic acid from cellulose by the action of *Coniophora cerebella* a hydrolytic split of 1,4-glycosidic bonds has been shown to be the initial step.

Nord and Vitucci (359) also made the interesting observation that methyl *p*-methoxycinnamate



is formed besides ethyl alcohol as a metabolic product, when the wood-attacking mold *Lentinus lepideus* is allowed to act on glucose or xylose. Acetaldehyde formed by dehydrogenation of the ethyl alcohol is an intermediate in the formation of the aromatic compound. This result may become of importance for the better understanding of the mechanism of lignin formation from carbohydrates in wood (cf. p. 320).

9. The Strength of Fibers; Degradation by Mechanical Means. Native cellulose fibers have considerable strength, as is indicated by the following figures for the tensile strength of various materials (360):

Substance	Tensile Strength kg./mm. ²
Cast iron.....	20 and more
Hardened spring steel.....	up to 170
Copper wire.....	up to 40
Aluminum.....	up to 10
Lead.....	up to 3
Wood, parallel to fibers.....	8-15
Silk.....	35
Cotton.....	28
Irish flax.....	> 100
Normal viscose.....	25
Viscose (highly oriented).....	up to 80
Normal acetate silk.....	18-20
Acetate silk (highly oriented).....	up to 100

Calculations of the tensile strength of a primary valence bond in a cellulose chain have given values between 800 and 2,000 kg./mm.² (361). This is, however, a simplified case, for as K. H. Meyer has emphasized, when the fiber is actually torn only a few of the many chains are torn *simultaneously*. The poorer the orientation in the direction of the fiber, the lower is its strength, as is shown by the figures quoted above. In some cases the chains are not so much broken as caused to slide past one another; this is particularly the case when the chains are short. In fibers which become weaker on being wet, such a sliding motion occurs in the wet fiber.

Native fibers actually show a higher strength when wet than when

dried (at a relative humidity of 65 %). This fact is demonstrated by the following figures of O. Schmidhäuser (362).

Fiber	Tensile Strength in kg./mm. ²			Ultimate Elongation %	
	Dry	Wet	Relative Wet Strength	Dry	Wet
Ramie.....	91-95	108	117	2.3	2.4
Cotton.....	20-80	24-83	105	6-12	6-13
Flax.....	84	88	105	1.8	2.2
Viscose.....	20-40	10-20	50	8-26	13-43
Viscose, highly oriented....	62	53	86	9	9
Cuprammonium staple fiber	23-33	15-20	65	17-20	17-30
Acetate staple fiber.....	16-21	10-12	65	21-30	29-30

A sharp decrease in strength is associated with the chemical degradation of cellulose, which leads eventually to the formation of the non-fibrous hydrocellulose. H. Staudinger and M. Sorkin (363) have carried out extensive measurements, using the apparatus of E. Franz and H. J. Henning (364). A decrease in the average degree of polymerization (DP) from 1,650 to about 700 did not cause a corresponding decrease in strength, but when the DP was further decreased to about 600, marked decreases were observed in both the tensile strength and the folding endurance. Degradation to a DP of about 250 caused the disappearance of practically all strength. The degradation is reflected particularly in the changes in the folding endurance.

Cellulose can be degraded by mechanical means, as well as by chemical ones. According to H. Staudinger and E. Dreher (365) it is not possible to cause depolymerization by beating in a Hollander beater, even if the pulp is "beaten to death." Grinding in an agate ball mill according to Bloch-Rosetti (cf. 365), on the other hand, causes extensive degradation. The following table illustrates this point.

Raw Cotton Degraded by Beating for Various Lengths of Time. Molecular Weight Determined by Viscosimetry in Schweizer's Solution at 20° C

Time of Beating	Degree of Polymerization	Physical Characteristics
Not beaten.....	1,360 1,400 1,500	Long-fibered; dissolves in Schweizer's reagent with much swelling. Eucolloidal
4 hours.....	830 850 960	Short-fibered; dissolves in Schweizer's reagent with swelling
8 hours.....	650 600	Short-fibered; dissolves in Schweizer's reagent with slight swelling
12 hours.....	370 380	Powder; dissolves in Schweizer's reagent without swelling. Mesocolloidal

E. Steurer (366) demonstrated that beating cellulose and polystyrene in the I. G. Farbenindustrie oscillating grinder "Vibrator" caused the lattice structure to be destroyed. The reactivity of the product was enhanced. The viscosity decreased sharply at the beginning of the beating and much more slowly thereafter. A chemical degradation of the molecule occurred; this was demonstrated by osmotic determination of the particle size.

In this connection we may recall the above-mentioned observation of K. Hess, H. Kiessig, and J. Gundermann (367) that when cellulose is ground in an oscillating grinder the X-ray diagram disappears, and that when the amorphous product of the grinding is heated with water, it becomes partially crystalline again as hydrate cellulose is formed.

C. COTTON CELLULOSE AND WOOD CELLULOSE

The chemical and physical properties of cellulose have hitherto been studied almost exclusively with cellulose from cotton. In the study of the chemistry of wood it is important to know whether the wood celluloses are identical with cotton cellulose. This question may be immediately answered by saying that so far as is now known, wood cellulose behaves like cotton cellulose, both chemically and physically. The first investigations of this matter were carried out by E. Heuser and A. Haug (368); they believed that cellulose was always the same definite chemical compound, no matter what its origin. E. Heuser and E. Boedeker (369) later supported this viewpoint with further experiments. Bleached sulfite pulp from spruce was purified with boiling 6 % alkali, which removed most of the impurities (pentosans), and the resulting product was saccharified with concentrated hydrochloric acid; the yield of sugar obtained was the same as that from cotton cellulose. L. E. Wise and W. C. Russell (370) have prepared cellobiose acetate both from sulfite pulp (spruce) and from cotton (both with and without purification with 17.5 % sodium hydroxide). The yield from cotton was 30.5 %, and that from spruce pulp, 27.4 % of the theoretical yield of acetate, calculated on the basis of the "normal cellulose." The normal cellulose is the residue of the raw material after treatment with 17.5 % NaOH. When the normal cellulose was acetylated directly, the yield of cellobiose averaged 28.4 % from the cotton and 28.3 % from spruce pulp. The same workers later extended these experiments to other kinds of woods (371). The celluloses were prepared by bleaching with chlorine and purifying with alkali, and were then subjected to acetolysis. The results are summarized in the following table:

Source of Cellulose	Yield of Cellobiose Acetate % of Theoretical	Melting Point of Cellobiose Acetate (Uncor.) (Average Value) ° C.
<i>Pinus lambertiana</i>	25.8	227.7
<i>Abies balsamea</i>	26.6	228.0
<i>Betula lutea</i>	28.2	227.8
<i>Picea rubens</i>	27.4	227.5
<i>Juniperus virginiana</i>	26.2	228.5
<i>Acer saccharum</i>	29.9	227.0
<i>Populus grandidentata</i>	23.9	227.5
<i>Tsuga canadensis</i>	24.7	227.0
<i>Fagus americana</i>	32.9	227.7
<i>Quercus alba</i>	25.7	228.2
Cotton	32.8-35.6	227.7

These figures show clearly that the yield from wood cellulose is somewhat smaller than that from cotton cellulose. This may well be due to the fact that it is never possible to prepare completely pure cellulose from wood. The removal of the pentosan is particularly difficult.

E. Heuser and W. Dammell (372), using the method of Wise and Russell, later prepared cellobiose in 28 % yield from spruce cellulose (sulfite pulp).

J. C. Irvine and his co-workers have given another method for identifying cellulose (373). They hydrolyze the completely acetylated polysaccharide with hydrogen chloride in methyl alcohol, obtaining acetylated sugar. This method was used to determine whether esparto cellulose consisted of a *mixture* of polysaccharides (each of which was made up of hexoses or of pentoses) or of *mixed* polysaccharides (built up of pentose and hexose residues). E. C. Sherrard and G. W. Blanco (374) subscribed to the latter view, so far as spruce cellulose was concerned. These investigators assume that the building units of the cellulose of spruce are *cellobiose* and *mannose* or *pentoses*. This point of view has been expressed even more definitely by Sherrard and S. S. Aiyar (375), who asserted that mannose is included in the make-up of this cellulose, which is therefore sharply differentiated from cotton cellulose. The basis of this statement was the fact that mannose had not at that time been isolated in the form of *mannan* either from spruce wood or from spruce cellulose, although celluloses isolated from the wood by drastic chemical means still contained mannose, and when mannose was dissolved out of the cellulose an equal or greater quantity of glucose went into solution. This idea that mannose is condensed with other carbohydrates to form cellulose is, however, incorrect, for K. Hess and M. Lüdtke (cf. p. 144) succeeded in isolating a mannan from sulfite pulp which was identical with that from ivory nuts.

E. Heuser and S. S. Aiyar (376) found, by using Irvine's method, that purified sulfite pulp and cotton cellulose both gave a pure triacetate in equal yields (circa 175 %). The α -methylglucosides were identical in the two cases, and were also obtained in equal yields.

Sulfuric acid hydrolysis of either wood cellulose or cotton by the methods of H. Ost and L. Wilkening (377) or of G. W. Monier-Williams (378) gave equal quantities (96 %) of crystalline glucose.

F. Lenze, B. Pleus, and J. Müller (379) determined the nature and amounts of the impurities in technical celluloses, with a view to gaining an understanding of the different behaviors of various pulps on nitration and subsequent working-up to powders. They observed that part of the so-called "wood gum," probably consisting chiefly of xylan, was very firmly linked to the cellulose [cf. also K. Fromherz (380)]. They even decided that "the action of hydrochloric acid (for the determination of pentosan) on cellulose which has been repeatedly treated with alkali causes the formation of a pentose complex, which then decomposes with the formation of furfural." This assumption certainly does not agree with the facts.

The observations of E. Schulze and C. Godet (381) are worth mentioning in this connection. They found that the xylan of the cell walls of seed husks was present in a form resistant to dilute mineral acids. Solution in cold 5 % sodium hydroxide caused the xylan to change into a form which was easily converted to xylose by boiling with 3 % sulfuric acid. F. Lenze and his co-workers (379) found the same thing to be true of the mannan in pulp, although this polysaccharide is not so firmly bound to the cellulose as is the xylan. This point is not very firmly established, however. Later experiments by E. Hägglund and F. W. Klingstedt (382) have made it appear very probable that the pentosan can be separated from the cellulose. The fact, that the residues obtained on alkali treatment in the previous experiments, on subsequent distillation according to Tollens' method, give volatile substances which condense with phloroglucinol, is due to the formation of hydroxymethylfurfural, which comes from the cellulose.

We shall return later to the interpretation of the fact that the pentosan (xylan) and perhaps also the mannan are hydrolyzed more or less readily by acids.

The idea that wood cellulose is identical with cotton cellulose is supported by the fact that wood cellulose yields a nitrocellulose which is very similar to that obtained from cotton (383). The cellulose acetates from wood and cotton are also quite similar, as has been shown by W. Nauck (384) and by E. Hägglund, N. Löfman, and E. Färber (385). It does appear, however, that cotton cellulose is originally less compact than wood cellulose, as is indicated by experiments of Hägglund and his co-workers.

The discovery of the crystalline structure of wood cellulose by R. O.

Herzog and W. Jancke (64) is of decisive importance. The Debye-Scherrer (386) X-ray method revealed the same interference pattern for wood cellulose as for cotton cellulose; this led to the conclusion that the same cellulose was present in the most widely-differing plants. The question as to whether the lignin was joined to the cellulose by adsorption or by chemical combination could not be answered, however.

On the basis of these results L. E. Wise (387) attempted to reconcile the two conflicting points of view by setting up the hypothesis that most of the elementary building blocks of wood cellulose are identical with those of cotton cellulose, but that other elements like mannan, pentosan, etc., are taken up by adsorption on the surface of the cellulose during growth, while the elementary particles of the cellulose are held together by secondary valences.

P. Klason (388) expressed the opinion that it would be advantageous to define wood cellulose in such a way that the properties which distinguish it from other polysaccharides would be emphasized. One such property is the insolubility at 98° C in bisulfite-hydrochloric acid (80 g. NaHSO_3 - 200 cc. N HCl per liter). Klason believed this cellulose to consist of two celluloses, cellulose I and cellulose II. The first is crystalline, while the second is amorphous. The latter in finely-divided form can be dissolved at 98° C in a solution containing 80 g. of NaHSO_3 in 500 cc. of N HCl, while the former is completely resistant to this reagent. The content of pentosan was evidently not considered by Klason. The composition of spruce wood may be given as an example: it was said to contain 47 % of cellulose I and 7 % of cellulose II.

Such a definition is no longer of any value. Cellulose obtained from beech still contains about 7 % of substances which yield furfural, according to Klason. These substances probably consist chiefly of pentosan.

E. Hägglund and F. W. Klingstedt (389) have also determined the rotations in cuprammonium solutions of bleached sulfite pulp of α -cellulose (derived from the pulp), and of cotton cellulose, and compared the values with one another. The measurements were made by the method of K. Hess. Several of Hess' values were included for purposes of comparison.

The constants of the celluloses were as follows:

A. Bleached Sulfite Pulp. Ash, 0.32 %; lignin, 0.42 %; Cu-number (according to Hägglund), 1.61; α -cellulose, 87.7 %; pentosan (determined with barbituric acid), 2.07 %; mannan (Hägglund-Klingstedt method), 3.23 %.

B. α -Cellulose. Free of pentosan and mannan.

C. Cotton. Ash, 0.19 %; α -cellulose, 95.17 %; free of pentosan and mannan.

α^{20} Observed. Obtained Graphically by Interpolation

Millimols. Cu	Millimols. Cellulose	α^{20}			Hess' Preparations	
		A	B	C	"Comparison Preparation"	"Wood Cellulose"
4.0	2.7	1.85	1.75	1.80	1.94	1.90
4.0	4.0	2.45	2.38	2.40	—	2.50
4.0	4.5	2.60	2.58	2.55	2.745	2.66
7.5	4.0	3.10	3.08	3.05	3.275	3.22
11.5	4.0	3.40	3.30	3.35	3.53	3.55

A comparison of the rotations of A, B, and C shows that these figures can not be used to distinguish wood pulps from one another or from cotton cellulose.

D. J. Bell (390) methylated α -cellulose preparations which had been obtained by chlorine- and alkali treatment of various woods, such as *Quercus pedunculata*, *Q. sessiliflora*, *Fagus silvatica* and *Picea sitkaënsis*. The maximum methoxyl content resulting from this treatment was 36.3-39.1 %, while cotton yielded a preparation containing 44.3 % of methoxyl under the same conditions. [P. Karrer and E. Escher (391) found that complete methylation of cotton cellulose gave a product with 42-43 % OCH_3 , which is less than the theoretical amount. When the starting material was partly degraded, e.g., when acetylcellulose was used, it was possible to secure a product with the theoretical content of methoxyl. It was concluded from these results that part of the hydroxyl groups of the cellulose are blocked by ether formation.] Hydrolysis of the methylated products from wood cellulose with hydrogen chloride in methyl alcohol yielded a residue with only 28 % of methoxyl. These results would definitely indicate a difference between wood cellulose and cotton cellulose. J. Barsha and H. Hibbert (392), using a large excess of the methylating agent, have obtained methylated products containing between 44 and 45 % of methoxyl from highly purified spruce and maple sulfite celluloses. The theoretical value for trimethylcellulose is 45.56 %. Hydrolysis of the methylated products gave good yields of trimethylmethylglucoside. According to these results, there is no difference between wood cellulose and cotton cellulose.

H. Staudinger and E. Dreher (393) have attempted to determine the degree of polymerization of the cellulose in wood. However, this cellulose is practically insoluble in Schweizer's reagent. Even a very lengthy treatment resulted in the solution of only 3 to 10 % of the cellulose, depending on the kind of wood. The degree of polymerization of this part of the cellulose was about 1,000. The remainder of the cellulose could be dissolved only after the lignin had been removed with chlorine

dioxide according to E. Schmidt (394); the degree of polymerization was 900-1,600.

Later investigations gave the following values for the average degree of polymerization (DP) of isolated wood celluloses (395):

Cellulose from	DP
Spruce (<i>Picea excelsa</i>).....	1,100
Pine (<i>Pinus silvestris</i>).....	1,000
Beech (<i>Fagus silvatica</i>).....	1,000
Birch (<i>Betula alba</i>).....	1,100
Maple (<i>Acer pseudoplatanus</i>).....	960
Alder (<i>Albus incana</i>).....	1,050
Musanga (<i>Musanga Smithii</i>).....	1,200
Black poplar (<i>Populus nigra</i>).....	1,200
Poplar (<i>Populus canadensis</i>).....	1,050
Aspen (<i>Populus tremula</i>).....	1,100
Silver poplar (<i>Populus alba</i>).....	1,000

According to these figures, the DP of wood cellulose is only about one-third that of cotton cellulose. W. Klauditz (396) obtained results appreciably higher than those of Staudinger. He isolated the celluloses with chlorine dioxide and pyridine, as well as with chlorine and alkali, and then treated them with 5% sodium hydroxide, and determined their viscosities, with the following results:

Type of Wood	Cellulose Obtained with Chlorine DP	Cellulose Obtained with Chlorine Dioxide DP
Beech (<i>Fagus silvatica</i>)...	1,730	1,910
Linden (<i>Tilia parvifolia</i>)...	1,780	1,970
Ash (<i>Fraxinus excelsior</i>)...	1,700	1,930

H. Dolmetsch and Fr. Reinecke (397) have determined the polymolecularity of various wood pulps by fractional solution of the corresponding nitrocelluloses and viscosimetric measurement of the chain lengths of the individual fractions. They found that wood pulps differ from cotton in that they are relatively more *polydisperse*. The DP of sulfite pulp from beech (prepared for artificial silk) was 1380-1550, that of spruce pulp was 1600-1780, while that of linters, 1690.

R. H. Blaker, R. M. Badger and R. M. Noyes (398) also found, that the nitrated celluloses obtained from wood pulps possessed a much higher degree of polymolecularity than those obtained from cotton linters. A similar result was obtained by N. Gralén (189).

On the other hand, the determination of the polymolecularity of nitrated wood cellulose by fractional precipitation and viscosimetric measurements lead R. L. Mitchell (399) to the conclusion that the cellulose in native wood is very similar to native cotton cellulose with respect to both length and uniformity of length of the molecules. According to

Mitchell about 50 % of the wood substance (Western hemlock and loblolly pine) consists of long-chain carbohydrates (α -cellulose) with a DP of 2,000-2,500. A group of wood polyoses, which is present in the wood to the extent of 20 %, has a DP of 70.

S. Coddick (100) reports that the DP of aspen cellulose is 4,370 in the wood. A value of 4,780 was found for cotton cellulose. Very high values had also been obtained by N. Gralén [(101), cf., however, p. 74]. From sedimentation-velocity experiments, carried out with nitrated celluloses prepared from spruce wood which had been sulfite-cooked under mild conditions, O. Bryde and B. Rånby (192) concluded that native wood cellulose has a weight average degree of polymerization of approximately 3,300.

D. THE DETERMINATION OF CELLULOSE IN WOOD

In 1910 M. Renker (102) published an extensive critical investigation of the methods then known for determining cellulose. He investigated cotton, jute, sulfite pulp, and wood. The last substance is of greatest interest here, and his results for this material will therefore be discussed briefly.

Methods in which the material is treated with strong hydrolyzing agents like dilute alkali or hot mineral acids in aqueous solution (Henneberg) or in glycerine (Gabriel, König), fused alkalies (Lange), or hot phenol (Bühler) are particularly unsuitable for the quantitative isolation and determination of cellulose in wood. Such treatment results in much decomposition, and the residues still contain remnants of lignin and pentosan.

The lignin is better removed by treatment of the wood with oxidizing agents like nitric acid, nitrous acid, potassium permanganate, hydrogen peroxide, etc. The use of such reagents is, however, attended with the danger that part of the cellulose may be converted into oxycellulose or other degradation products, which will then dissolve on subsequent treatment with alkali.

Chlorine and bromine, which are particularly suited to the removal of the lignin from wood, are often considered to belong to the group of oxidizing agents, but their action is not primarily an oxidation, but a halogenation with oxidation as a possible sidereaction. Chloro- and bromolignins are insoluble in water and therefore form a layer on the surface of the wood which has to be removed with sodium sulfite before the reagent can penetrate into the wood. Hence it is necessary to repeat the operations of chlorination (bromination) and solution of the chlorinated (brominated) lignin until no further reaction can be observed. The taking

up of halogen is widely believed to be solely a substitution reaction (403). This results in the formation of hydrochloric or hydrobromic acids, which must be removed to prevent damage to the fibers. High yield of cellulose can be obtained in this way, but the cellulose thus obtained is not pure; it consists of a mixture of cellulose and of wood polyoses which are resistant to chlorine—pentosan, in particular. The amount of pentosan is often subtracted to determine the true content of cellulose, but it must be emphasized that this does not give the true weight of cellulose, since other polysaccharides besides pentosan are present in the residue (mannan, laevulan, etc.). When the chlorination is conducted in such a way that the formation of oxycellulose is kept to a minimum, the residue contains not only all the cellulose, but also the chlorine-resistant wood polyoses.

C. F. Cross and E. J. Bevan (404), who first proposed chlorination as a method of determining cellulose, give the following directions, which may well be quoted, in view of the fact that the method has also been used by many other investigators:

The material is cooked for $1\frac{1}{2}$ hour with 1 % NaOH, washed, and treated for $1\frac{1}{2}$ -1 hour with chlorine gas while it is moist. The residue is washed one or two times with water to remove the hydrochloric acid which is formed. A 2 % solution of Na_2SO_3 is then poured over the mass, and it is slowly brought to boiling, treated with 0.2 % of its volume of NaOH, and kept at the boiling point for five minutes longer. The material is again washed with hot water, and bleached with 0.1 % KMnO_4 solution. Any MnO_2 which precipitates is removed with SO_2 . The mass is now thoroughly washed, dried, and weighed.

A. L. Dean and G. E. Tower (405) call attention to the fact that a single treatment according to these directions is not sufficient to remove all the lignin. Only after three repetitions did the lignin reaction with phloroglucinol become quite weak. M. Renker (406) found that six treatments are required. They also found that the cellulose was attacked when the process was repeated; it is clear, therefore, that in this determination one has to choose between a final product which contains lignin, but has not been very much attacked, and a lignin-free product which no longer contains all the cellulose (407).

Various proposals for modifying the procedure have been made from time to time. M. Renker (408) was induced by earlier studies of E. Fremy and A. Terreil (409) to try using chlorine water in various concentrations, but found no advantage in this (410). The use of "nascent" chlorine from a mixture of potassium permanganate and hydrochloric acid was even less successful. G. J. Ritter and R. L. Mitchell (411) have also proposed improvements, without really making any fundamental changes in the method.

H. Müller (412) reported a method for determining cellulose by delignification with bromine water, as early as 1877. His method has been widely used, but it suffers from the same difficulties as does the chlorine method described above:

Two g. of the material is cooked thoroughly with water, and then treated with 100 cc. of water and 5-10 cc. of a solution containing 4 g. of bromine per liter. As soon as the yellow color of the bromine disappears, fresh bromine solution is added, and this process is continued until the yellow color is stable for 12-14 hours. The residue, after being washed, is treated with hot, dilute ammonia (4 cc. per liter), until no more bromolignin is dissolved. This procedure is repeated until the fibers are perfectly white.

In the case of wood it is necessary to carry out the above operations nine to twelve times in order to obtain fibers free of lignin; this requires a very long time. The reason for this is, as in the case of the chlorine method, that the surface layer of insoluble bromolignin prevents the penetration of the bromine into the interior.

Even if a lignin-free fiber is finally obtained in this way, the residue is not a pure cellulose, but a product containing much pentosan and other wood polyoses.

None of the methods based on oxidation in aqueous solution are of much value. These methods include the use of KMnO_4 in alkaline or acid media, or in the presence of chlorine [Renker (413) Cross and Bevan (414)] or nitric acid [S. Zeisel and M. J. Stritar (415)], the use of nitric acid alone [G. J. Mulder (416), Cross and Bevan (417)], nitric acid plus potassium chlorate [F. Schulze (418) and W. Henneberg (419)], nitrous acid [Cross and Bevan (420) and C. G. Schwalbe (421)], potassium chlorate and chlorine [W. Hoffmeister (422)] or sodium hypochlorite [M. Renker (423)]. The reason is that although the lignin is easily degraded by oxidizing agents, the cellulose is also attacked and partially converted into oxycelluloses. This is clearly reflected in the high copper number which results.

There are also several methods which involve oxidation and hydrolysis. They are likewise of no value for exact determinations of cellulose. J. Lifschütz (424) combines sulfuric and nitric acids, J. König (425) uses sulfuric acid in glycerol and hydrogen peroxide, O. Simon and H. Lorisch (426) use potassium hydroxide and hydrogen peroxide, B. Tollens and R. Dmochowsky (427) use dilute sulfuric acid and potassium hydroxide successively, and oxidize with nitric acid, and F. A. Bühler (428) employs phenol to extract the lignin and potassium permanganate to bleach the residue.

The delignification with acid sulfite, first used by C. Counciler (429), but

carefully studied only by P. Klason (430), is not to be classified with any of the above groups of methods. This method is not practicable for cellulose determinations because it requires too much time; the directions will nevertheless be given:

The original directions of P. Klason were as follows: The substance is treated for 24 hours at 108° C. with a solution 0.5 N in CaSO_3 (or MgSO_3) and 0.6 N in SO_2 , after which the residue is purified with bromine for approximately one week, by the procedure of H. Müller (412).

This method did not give satisfactory results, and Klason has therefore modified it, although the principle of the old method is retained (431).

Not more than 10 g. of wood, cut into pieces 1 cm. long and as thick as match sticks, is put into a 150 cc. pressure flask and covered with 100 cc. of a liquor containing 80 g. of sodium bisulfite and 200 cc. of N HCl per liter. The mixture is heated in a steam cabinet at about 98° C until the residue no longer loses weight. The liquor is changed every fourth day.

Investigation of wood from a spruce tree 100 years old gave the following results:

Duration of Cooking, Days	Undissolved %	Sugar (Hemicellulose) in Solution, after Inversion %	Lignin Dissolved %
1	81.54	9.78	6.68
2	74.00	11.86	12.14
3	69.04	12.04	16.70
4	68.96	—	—
5	62.05	13.62	22.33
6	63.83	12.84	22.03
7	57.18	—	—
8	55.44	—	—
11	54.19	—	—
14	54.98	14.31	28.71
15	55.40	14.09	28.51
16	53.74	14.70	29.54
19	54.03	—	—
21	53.75	14.42	29.81

The cellulose content of spruce wood, according to the definition of P. Klason (388) is therefore about 54 %. No account is taken of the pentosan content; the difficulties which such a viewpoint involves have been discussed above. The method of Klason, therefore, can not be used, either, for exact determinations of cellulose. The content of cellulose can not even be determined indirectly by subtracting the content of pentosan and assuming that the cellulose is not attacked by the weakly acid bisulfite. The latter assumption is quite justified, since cotton cellulose remains intact when it is so treated (432), but there remain mixed with the cellulose not only pentosan, but also other polysaccharides, as has been mentioned already and as will be discussed in more detail below. E. Hägg-

lund and F. W. Klingstedt (433), taking these factors into account, have estimated that spruce wood contains about 41 % of cellulose.

The following summary, taken from Renker's work (402), shows how variable are the results obtained when the cellulose content of spruce wood is determined by the methods mentioned below:

Method	Yield %	Purity of the Cellulose		
		Lignin Reaction	Pentosan Reaction	Extent of Attack on the Cellulose
Cross and Bevan Cl	60.6 (6 treatments with Cl)	Negative	Strong	Some oxycellulose Cu No. 3.0
Cross and Bevan Cl	64.6 (3 treatments with Cl)	Faint	Strong	—
Müller Br	58.0-59.9	Negative	Strong	Some oxycellulose Cu No. 3.0
Renker KMnO ₄ + Cl	43.0	Negative	Strong	Much oxycellulose Cu No. 5.1
Zeisel and Stritar KMnO ₄ + HNO ₃	40.2	Positive	Strong	Much oxycellulose Cu No. 10.7
Mulder HNO ₃	53.6	Negative	Strong	Oxycellulose Cu No. 4.5
Schulze-Henneberg HNO ₃ + KClO ₃	49.6-58.1	Negative	Strong	Oxycellulose Cu No. 3.7
Renker NaOCl	50.5	Faint	Strong	Much oxycellulose Cu No. 13.4
Schwalbe HNO ₂	55.8	Negative	Strong	Oxycellulose Cu No. 4.0
Hoffmeister KClO ₃ + Cl	57.2	Negative	Strong	Oxycellulose Cu No. 5.8
Lifschütz H ₂ SO ₄ + HNO ₃	43.4	Negative	Strong	Much oxycellulose
König glycerol-H ₂ SO ₄ + H ₂ O ₂	37.2-44.2	Negative	Negative	Much attacked
Bühler phenol and KMnO ₄	51.9	Negative	Weak	Cu No. 2.6
Klason-Counciler Ca (Mg) bisulfite + SO ₂ at 108° C (+ Br)	50.6-55.8	Faint	Strong	Uncertain
Klason Na bisulfite + SO ₂ at 98° C	54	Negative	Strong	None

It should be pointed out that a negative lignin color reaction in the cellulose preparations obtained by the methods summarized in the table does not necessarily mean that there is no lignin present. A negative result of the color test may simply be due the fact the coniferaldehyde

groups, which are responsible for the color reactions of lignin, may have been destroyed by the oxidants, or blocked by the addition of bisulfite, in the Klason methods (cf. p. 189).

Of the other investigations, the work of L. Kalb and V. Schoeller (434) deserves mention. This work was based upon the experiments of Bühler, and consisted in delignification with phenol in the presence of small quantities of mineral acids. Heating for one hour on a water bath with phenol containing 0.1 % of HCl gave a yield of 48.3 % of cellulose from spruce, and 46.4 % from beech. The contents of pentosan were 4.6 and 7.9 %, respectively. Another method, due to K. Kürschner and A. Hoffer (435), involves the refluxing of 1 g. of wood chips (freed of resin) with 25 cc. of a mixture of 5 cc. of nitric acid (d. 1.4) and 20 cc. of ethyl alcohol. The residue is filtered off after one hour and the treatment is repeated a time or two. This causes by far the larger part of the hemicellulose of the wood to be dissolved out. This method is, however, no more suited than those described previously for the *direct* determination of the cellulose content.

N. S. Koslow, L. E. Oliphson, and S. M. Goldina (436) attempted to determine cellulose quantitatively by the method of E. Wedekind and O. Engel (437), in which the wood is treated with *dioxane*. The results obtained were compared with those given by the method of K. Kürschner (438). The procedure was as follows: sawdust was extracted in a Soxhlet first with water, and then for six hours with a mixture of equal parts of alcohol and benzene. It was then dried, and 1 g. of the dry product was heated to 90-95 °C for 6 hours with 15 cc. of dioxane plus two or three drops of 0.04 % hydrochloric acid, under reflux. (The dioxane has practically no action in the absence of hydrochloric acid.) The yield was 55 %, or approximately the same as that obtained by Kürschner's procedure. The residue did not consist of pure cellulose, however, but contained other carbohydrates and some lignin; it is therefore necessary in this procedure, too, to subtract the quantities of impurities in order to determine the true cellulose content.

In order to determine the *true content of cellulose* it is necessary to determine the hemicellulose which accompanies the cellulose. E. Hägglund and his co-workers (439) attempted to do this in the following manner, in the case of spruce wood:

Wood in the form of small pieces or chips was treated for 10 hours at 130 °C with five times its weight of an "impregnating liquid" containing 8 g. of Na_2SO_3 and 6 g. of NaHSO_3 per 100 cc. After cooling, two-thirds of the liquor was drawn off, and replaced by 6 % SO_2 water. The cooking was finished in another 2½ hours at 130 °C. The pulp was freed of liquids,

fiberized, and washed with water. The large quantities of solid lignosulfonic acid which remained were mostly removed by the method of C. Kullgren (440), as follows: the pulp was allowed to stand for 12 hours at room temperature with 0.2-0.3 *N* hydrochloric acid, and then washed on a Buchner funnel with an equal quantity of acid of the same concentration. The hydrochloric acid was removed by washing with distilled water. The material was allowed to stand for 20 hours with ethyl or methyl alcohol, which dissolved the resins. After the alcohol had been removed, the lignin was dissolved out with boiling alcohol for 10 hours, the solution drawn off, and replaced with fresh alcohol, and the extraction continued for another 15 hours. Not all the lignin is thus removed; 2-3 % of it remains behind, but it may be removed by treatment with bleaching powder (calcium chloro-hypochlorite). The bleaching is best carried out in a 5-6 % suspension of the pulp, and at a temperature of 35°C. The bleaching powder is added a little at a time, as the chlorine is used up. The bleaching process is finished in 8-10 hours.

The hemicellulose fraction of the pulp was determined after complete saccharification of the pulp. Only the pentosan was determined directly. Fifteen grams of air-dried material was treated with 130 cc. of 72 % sulfuric acid. It is advisable to evacuate the mass in order to obtain good mixing. After four hours the solution was diluted to 400 cc., and allowed to stand 6 hours more at room temperature. The volume was now brought to 5 liters by dilution with water, and the mixture refluxed for 6 hours. After this time the reductive power of the solution no longer increased, and sugar equal to 102-105 % of the pulp was present, as determined by the reductive power (theoretical is 111 %). This result may be considered satisfactory. The excess of sulfuric acid was removed with chalk, and the slightly acid solution was concentrated to 750 cc.

Mannose in the solution was determined as follows: 75 cc. of the solution was placed in a 100 cc. glass-stoppered Erlenmeyer flask, a few crystals of sodium acetate were added, and sufficient phenylhydrazine in acetic acid solution was added to give a weight of phenylhydrazine equal to the total weight of the sugars in solution. (The phenylhydrazine solution contained 1.6 cc. of 25 % acetic acid per cc. of phenylhydrazine and was always freshly prepared.) The mannose must not be less than 10 % of the total sugar, or the mannose phenylhydrazone will not be completely precipitated; this content of mannose is assured by weighing out this quantity of mannose and adding it to the solution. After the addition of the phenylhydrazine solution, the flask was filled with water and allowed to stand at room temperature for 15-20 hours, after which the hydrazone was filtered off on a sintered glass crucible and washed with 15 cc. of ice

water, 10 cc. of absolute alcohol, and 10 cc. of ether. The color changed from yellow-brown to light yellow on washing. The precipitate was dried over phosphorous pentoxide in a vacuum. The purity of the hydrazone was checked by taking a melting point.

Galactose was determined as follows: 100 cc. of the sugar solution was treated with the same volume of alcohol, which caused most of the calcium sulfate present to precipitate out. The filtrate was concentrated to 5 cc. and treated with 60 cc. of nitric acid of d. 1.15. The solution was evaporated to exactly 20 cc., and treated with 500 mg. of mucic acid. After standing at 15° C for 48 hours, the precipitate of mucic acid was filtered off in an alundum crucible, and washed with 20 cc. of a mucic acid solution which was saturated at 15° C. The precipitate was finally washed with 5 cc. of cold water (441).

Fructose was determined colorimetrically by the method of Seliwanoff. A qualitative test was made for uronic acids by the naphthoresorcinol method of Neuberg. Pentosans were converted to furfural in the usual manner by a Tollens distillation, and the furfural was precipitated by barbituric acid.

The following results were obtained:

Yields in Per Cent of the Weight of the Wood

	Expt. 1	Expt. 2	Expt. 3
Pulp resulting from the original cooking.....	69.6	69.0	61.6
Yield after extraction according to Kullgren	54.6	55.8	50.6
Yield of bleached pulp.....	52.0	52.7	48.1
Yield of α -cellulose.....	41.8	42.2	40.1
Hemicellulose and ash in the bleached pulp.....	8.8	10.4	5.3
Cellulose (with possible admixture of glucan)....	43.2	42.3	42.8
Hemicellulose and ash in the α -cellulose.....	0.6	2.4	0.6
α -cellulose, free of hemicellulose.....	41.2	39.8	39.5

In the third experiment the cooking with sodium sulfite was carried out in the technical way. A 14 % NaHSO_3 solution was used, and the cooking allowed to proceed for 8 hours at 140° C, with a heating period of 5 hours. The lignosulfonic acid of the pulp was dissolved out with water at 80° C, instead of with alcohol.

From these figures it may be seen that the cellulose content of spruce wood is between 42.3 and 43.2 % of the weight of the wood. It is possible that this figure includes several percent of difficultly hydrolyzable glucan (cf. p. 148). The maximum content of α -cellulose, free of hemicellulose, is 41.2 %. Since a value of 41.5 % was found earlier (442) on analysis of a "strong" sulfite pulp, prepared in a technical cook, it is evident that cellulose is not degraded under these conditions.

The cellulose content found by H. Staudinger and E. Husemann (443)

agrees well with this figure. They determined the cellulose by treating the wood with chlorine dioxide (or acid sodium chlorite) according to E. Schmidt (444). The residue (the "skeletal substance") was then treated with 8-10 % sodium hydroxide in order to remove the wood polysaccharides (hemicellulose) from the cellulose. The following results were obtained:

Type of Wood	% Residue			% Cellulose		
	I	II	III	I	II	III
Spruce (<i>Picea excelsa</i>).....	60.6	61.0	61.3	41.0	41.5	42.0
Pine (<i>Pinus silvestris</i>).....	62.0	62.5	62.6	39.7	40.3	40.2
Beech (<i>Fagus silvatica</i>).....	65.4	61.7	65.9	37.7	37.5	37.3
Birch (<i>Betula alba</i>).....	64.2			38.5		
Maple (<i>Acer pseudoplatanus</i>)..	64.4			38.2		
Alder (<i>Alnus incana</i>).....	71.4			39.6		
Linden (<i>Tilia parvifolia</i>).....	71.6	70.0		38.6	37.5	
Musanga (<i>Musanga Smithii</i>)..	63.0	64.2		41.0	40.8	
Poplar (<i>Populus canadensis</i>)..	68.0	67.3		44.8	45.4	
Aspen (<i>Populus tremula</i>).....	68.0	68.5		41.8	42.4	
Silver poplar (<i>P. alba</i>).....	64.0	71.2		40.3	41.0	
Black poplar (<i>P. nigra</i>).....	69.7	73.0	73.6	50.3	50.4	51.0

This method of determining the cellulose has the advantage of great simplicity. It must be understood that the treatment with alkali may possibly cause the lower molecular part of the cellulose (DP less than 100) to be lost. In fact, the analyses of Hägglund quoted above show that the cellulose content of spruce wood, including the alkali-soluble "glucan", is 2-3 % higher. In order to be certain of the results it is necessary to carry out a simultaneous pulping with bisulfite, and to remove the lignin from the bisulfite pulp by mild bleaching. Later investigations have shown that it is advantageous to carry out this bleaching with chlorine dioxide, since damage to the fibers and degradation of the cellulose are more easily avoided than when hypochlorite is used (445).¹

When the holocellulose is prepared with acid sodium chlorite by L. E. Wise's (447) modification of Jayme's method, a subsequent extraction with potassium hydroxide in concentrations up to 24 % KOH does not completely remove the wood polyoses (448). The resulting "α-cellulose" then contains appreciable amounts of mannan, xylan, and polyuronides. If a correction is made for these substances, there results a figure for "true cellulose" which supposedly consists only of long chains of glucose residues. The values were relatively high, being 48.3 % for Douglas fir, 45.6 % for black spruce, and 40.6 % for Overcup oak. It is possible that

¹ There are good reasons for believing that the degradation goes still farther when the pulping is carried out with dilute nitric acid; remarkably low α-cellulose values are then obtained (446).

this procedure does not attack certain wood polyoses which the method of E. Schmidt either dissolves or so alters that they go into solution during the alkali extraction. Only in this way can the differences from the values of Staudinger be explained.

In a method described by L. E. Wise, F. C. Peterson, and W. M. Harlow (449), the wood is treated with hot ethanolamine. The finely-divided wood is treated with 50 times its weight of ethanolamine for 5 hours at 168° C (the boiling point). The residue is treated first with chlorine water and then with sodium sulfite. A yield of 60.5 % was obtained from beech. In the case of softwoods the extraction of lignin proceeds obviously not so smoothly (450).

G. Jayme and P. Schorning (451) have used the following method for the determination of the content of "resistant pure cellulose" in beech wood. About 5 g. of sawdust is heated to 80° C for 1½ hours with 3.5 % nitric acid, with the addition of 0.45 mg. of NaNO₂. The residue is digested for an hour at 50° C, with a solution containing 2 g. NaOH and 2 g. Na₂SO₃ in 100 cc. of water. After being washed and acidified, the residue is bleached at 35° C with a sodium hypochlorite solution containing 5 % active chlorine and 1 % NaOH (on the basis of the weight of the residue). The cellulose is finally treated with mercerizing liquor (17.5 % NaOH) at 20° C. The cellulose prepared in this way from beech wood yielded 1 % of furfural and 0.3 % of methoxyl. The yield of cellulose was not the same for all samples of wood, as may be seen from the following table [G. Jayme and F. Reh (452) also found that the cellulose content of black poplar, *Populus monilifera*, varied considerably with the age of the wood. The cellulose content decreased from about 50 % to 44 % as the age increased from 17 to 43 years; this is due primarily to the increase in lignin content.]

Age, years	Quality	Content of "Resistant Pure Cellulose" in %		
		Place on Trunk 0.1-0.5 m. Above the Ground	5-12 m.	Average
30	I—II	33.71	35.06	34.39
43	III	35.44	35.74	35.59
86	IV—V	34.76	35.90	34.83
86	III—IV	34.65	36.70	35.68
86	III	35.53	36.19	35.86
108	I	36.90	36.75	36.83
114	III	35.88	35.51	35.65
114	IV—V	35.81	35.11	35.46

The average degree of polymerization of such cellulose was 650. The cellulose chains have therefore been shortened; Staudinger and Husemann (453) attribute this to the action of the bleach. The alkali-solubility is

thus increased, and this explains why the yield of alkali-resistant cellulose (α -cellulose) is 1-2 % less than that obtained by the method of Staudinger and Husemann mentioned above (443).

W. Kladitz (454) obtains higher yields of cellulose; the yield of pentosan-free cellulose, insoluble in 10 % sodium hydroxide was 41.8 % when beech was digested with chlorine dioxide, and 40.56 % when it was digested with chlorine. G. Jayme and F. Fink (455) have recently reported the content of pure cellulose in spruce wood to be 45 %.

P. F. Cundy and M. M. Beck (456) found considerably higher values for α -cellulose in unbleached wood pulp than in the same pulp after removal of the lignin by treatment with sodium chlorite. The authors explain this by the assumption that in the unbleached pulp some part of the hemicelluloses is protected by the lignin. Obviously, true values for alkali-resistant cellulose are obtained only after the lignin has been completely removed.

It is evident that the yield of cellulose depends very much upon the method of isolation.

III. Wood Polyoses and Polyuronic Acids

A. NOMENCLATURE

The water-insoluble polysaccharides which accompany many celluloses and which are easily saccharified by dilute mineral acids have been termed *hemicelluloses* by E. Schulze (457), as has already been mentioned. This definition does not, however, fit all the polysaccharides which are found together with the cellulose in wood, for it has been found that some of the non-cellulose polysaccharides are no more easily attacked by dilute acids than is cellulose itself (458). Indeed it is quite impossible to separate the hemicellulose from the cellulose by acid hydrolysis without causing extensive degradation of the cellulose (459).

P. Karrer (460) has suggested that a better system would be to classify all polysaccharides *according to the sugars which they gave on complete hydrolysis* and then to form subgroups *according to the physiological rôle which the polysaccharides play*, as follows:

Hexosans

Physiological Rôle	Glucans	Fructans	Mannans	Galactans
Skeletal substance	Cellulose		For example, mannans from certain cell walls	For example, galactans from certain seed coatings
Reserve substance	Starch Glycogen Lichenin	Inulin	Mannan in ivory nuts and carob bean seeds	Galactans in the reserve food of seeds

<i>Pentosans</i>			
Xylan		Araban	Araboxylan
Structural xylans		Structural arabans	—
Reserve xylans		Reserve arabans	—
<i>Hexosanpentosans</i>			
Galacto-araban	Gluco-araban	Galacto-xylan	Gluco-xylan

Besides the groups listed above, there are some in which two different hexoses may be associated, as for instance, galactomannans, fructomannans, etc. In the case of these polysaccharides it is not clear whether a carbohydrate built up of mannose and galactose residues is really present, or whether it is only a mixture of mannan and galactan.

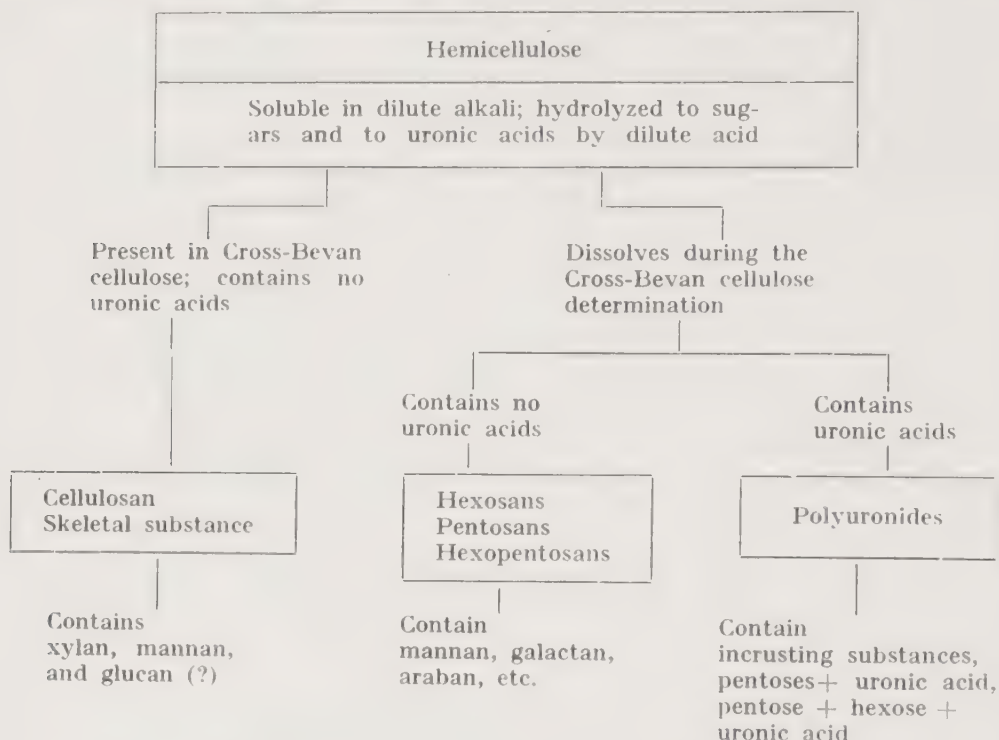
Because of this circumstance, H. Staudinger and F. Reinecke (461), have proposed the term *wood polyoses* as one which is suitable for *all the polysaccharides* of the lignified cell (except cellulose).

The old designation does not eliminate confusion; the "hemicellulose" is, for example, more or less soluble in alkali. Alkali-solubility is also characteristic of the degradation products of cellulose present in so-called β - and γ -cellulose.

Pectins and polyuronic acids were formerly included with the "hemicelluloses." However, these compounds can hardly be classified as wood polyoses. As far as their quantities are concerned, they are definitely of secondary importance; E. J. Candlin and S. B. Schryver (462) found only traces of pectin in wood. *Non-lignified* tissues contain relatively large amounts of pectin, but no lignin, and, oddly enough, no wood polyoses. These authors propose the designation *polyuronides* for "hemicelluloses" which contain uronic acids and which are linked to sugar anhydrides.

No one has yet succeeded in achieving a clear-cut separation of the various polyoses and polyuronic acids which occur in wood. L. F. Hawley and A. G. Norman (463) have proposed dividing the "hemicelluloses" into two groups: first, those which are only loosely bound to the cellulose, and second, those which are closely connected with the cellulose. According to Hawley and Norman, the two groups can be separated by the Cross-Bevan method for determining "cellulose." Those substances which contain uronic acids and which go into solution during this determination are designated as polyuronides. No generic term has yet been given to the hexosans, pentosans, and hexopentosans which contain no uronic acids. That part of the hemicellulose which is not separated from the cellulose by the Cross-Bevan procedure is called *cellulosan*. It contains no uronic acids.

The complete classification of the "hemicellulose" according to this scheme is as follows:



This classification is by no means obvious. It appears questionable that only that part which is called "cellulosan" is to be reckoned among the "skeletal substances" of the wood. E. Schmidt and his co-workers (444) have made a series of attempts to prove that chlorine dioxide is a reagent which separates wood into "skeletal substances" and "incrusting substances." When the Cross-Bevan chlorine-alkali method is used, it is impossible to avoid attack on the "cellulose" component (464); this would mean that not only the lignin, but also those carbohydrates which are in some way connected with the lignin, would be considered as "incrusting substances." Furthermore, it might be expected that for each type of wood a definite dividing line could be drawn between those substances which went into solution, and the residue. This is, however, not the case; the yield of skeletal substances appears to be very much dependent on the method of extraction of the wood after it has been treated with chlorine dioxide or with chlorine. If one proceeds with extreme caution it is indeed possible to isolate *all* of the carbohydrates present in the wood. G. J. Ritter and E. F. Kurth (465) were able to remove the lignin from maple and spruce without having any carbohydrate go into solution.

There is, therefore, no sharp boundary between skeletal substances

and incrusting ones; the American workers have therefore introduced the term "*holocellulose*" instead of skeletal substances for the carbohydrates concerned. Holocellulose includes both cellulose and wood polyoses, in this case.

Concerning the molecular weight of the wood polyoses, the previously mentioned work of R. L. Mitchell (399) (cf. p. 123) may be quoted. According to this work, the polyoses occurring in Western hemlock and loblolly pine to the extent of about 20 %, have an average DP of 70. They are much more low-molecular than the α -cellulose, the average DP of which was found to be 2,000-2,500.

Reviews concerning the utilization of hemicelluloses as well as their importance for the properties of paper have been published by G. Jayme (466) and L. E. Wise (467). The latter author has also given a review dealing with the chemistry of the hemicelluloses (467 a).

B. THE INDIVIDUAL WOOD POLYPOSES, THEIR PROPERTIES AND THEIR OCCURRENCE IN DIFFERENT WOODS

I. Pentosan. T. Thomsen (468) extracted wood with sodium hydroxide at ordinary temperatures, and thus isolated carbohydrates which he designated as *wood gum*. J. A. Poumarède and L. Fiquier (469) had already obtained this substance, but had mistaken it for pectin.

Thomsen's procedure was as follows: finely-grated wood was treated for 24 hours with water at room temperature, then washed with water, alcohol, ether, alcohol, water, ammonia-water, and finally with water again. The material was then digested for 24 hours with 30-50 times the quantity of 10 % sodium hydroxide. The wood gum dissolved was precipitated with two volumes of alcohol, dried, and weighed. The following results were obtained:

Kind of Wood	Per Cent of Wood Gum	
	From Wood Near the Bark	From Wood Near the Center of the Trunk
Birch.....	13.9	19.7
Beech, old.....	8.2	15.9
Beech, young.....	11.9	11.3
Beech, young.....	13.8	15.9
Ash.....	9.7	10.7
Elm.....	8.9	12.0
Oak.....	14.4	10.7
Cherry.....	19.3	15.4

Spruce gave less than 0.8 % precipitate, and an American fir, only 0.5 %. Thomsen concluded that softwoods did not contain wood gum. The elementary composition of the gum corresponded approximately

to the empirical formula $C_6H_{10}O_5$; the gum was therefore to be considered as a *hexosan*. After hydrolysis with dilute sulfuric acid the solution was strongly reducing, but it could not be fermented. F. Koch (470) later confirmed this point. The specific rotation for the sodium D line of the sugar obtained by hydrolyzing the gum was 20.2° . H. J. Wheeler and B. Tollens (471) later found that the gum was not a hexosan, but a *pentosan*. They named the sugar obtained from it by hydrolysis, *xylose* ($[\alpha]_D = -18-19^\circ$). In their experiments they used 5% sodium hydroxide, acting for 48 hours; this gave a smaller yield of gum, amounting to about 5% from beech, and only 0.4 % from fir.

The substance here designated as wood gum is probably nothing but *xylan*. A. W. Schorger (472) investigated how the yield of xylan varied with the concentration of alkali. Resin-free aspen wood was extracted for 48 hours with sodium hydroxide solution, then extracted again for 24 hours, and once more, for 18 hours.

Strength of Alkali %	Extraction No.	% of Wood Dissolved	Pentosan in Residue	
			%	% of the Total Pentosan
5	1	31.29	8.62	25.82
	2	3.38	6.82	19.42
	3	1.68	6.71	18.62
2	1	27.82	11.58	36.44
	2	2.52	9.67	29.37
	3	1.71	9.23	27.34
1	1	24.64	16.01	52.60
	2	3.57	13.58	42.50
	3	1.69	12.58	38.14

The methods of isolating pentosans have been improved in the course of time (473). It is questionable if anyone has ever succeeded in isolating pure xylan from wood, for so far as is known all the preparations, so far investigated, yielded arabinose on hydrolysis (474). Uronic acids have also been shown to be present, and even the most carefully purified preparations contain methoxyl (475).

K. Freudenberg, H. Molter, and G. Dietrich (476) succeeded in isolating xylose and arabinose in the pure state from the wood polyoses contained in acid hydrolyzates of beech and spruce. The separation of these sugars from the others was achieved by distillation of their diacetone derivatives. Xylose was separated from arabinose by transforming the diacetone-xylose into the monoacetone derivative without changing the diacetone derivative of arabinose. The yield of xylose from beech was 8-10%, and that of arabinose 0.3-0.4 % of the wood. The total amount of xylose in beech wood was computed to be 18%, and that of

arabinose, 0.5%. From corresponding hydrolyzates of spruce wood only 1.4% of xylose and 0.7% of arabinose, calculated on the weight of the wood, were isolated. Xylose, in a yield of 4-5 g. per 100 g. of wood, was also prepared from the sulfite waste liquor of beech wood.

Investigations in Hägglund's institute (477) have shown that the spruce wood polyoses hydrolyzable at pH 2 yield 16 g. of sugars per 100 g. of wood, after complete hydrolysis. The sugar mixture contains xylose in a quantity corresponding to 5% of the weight of the wood, and arabinose equivalent to 0.8%. These figures are, within the experimental error, equal to those of Freudenberg and his co-workers (476).

E. Schmidt and E. Graumann (478) were the first to show that the isolation of xylan from wood is made easier by pre-treatment with a 0.25% chlorine dioxide solution. Subsequent treatment with 0.2% sodium hydroxide solution gives an easily soluble xylan, according to Schmidt, and further extraction with 5% alkali yields a difficultly soluble xylan. Schmidt says that the difficultly soluble xylan carries *acetyl groups* which are bound as esters (479). He further states that not only acetyl groups, but also *methoxyl* groups are present in the xylan of hardwoods; the acetylxylan is supposed to be particularly extensively methylated (1.44% methoxyl).

According to Schmidt the hardwoods show integral relationships between the quantities not only of cellulose and acetylxylan, but also among the acetyl, methoxyl, and carboxyl groups, as follows (480) (concerning the carboxyl content of cellulose see, however, p. 46):

Components	Ratio
1. $C_6H_{10}O_5$ of cellulose to $C_5H_8O_4$ of acetylxylan	3:1
2. $C_5H_8O_4$ of acetylxylan to $COCH_3$ of skeletal substance	1:1
3. Carboxyl of cellulose to carboxyl of deacetylated xylan	1:2
4. CH_3O of cellulose to CH_3O of deacetylated xylan	1:2
5. Carboxyl to methoxyl of cellulose	1:1
6. Carboxyl to methoxyl of acetylxylan	1:1

W. Voss and his co-workers (481) investigated the xylans of various plant membranes, e.g., in beech wood, seed coverings from plum and cherry stones, and walnut shells. A fractionation according to E. Schmidt was carried out, giving portions soluble in 0.2% and in 5% NaOH, respectively. The latter fraction is, according to Schmidt, the part which is completely coupled to cellulose. This fraction was found to be the same, no matter what its source. Voss was able to demonstrate that xylan is not composed entirely of xylose, but also [as W. N. Haworth (474) had already found in the case of esparto grass] of arabinose; 1 molecule of arabinose occurs for every 8 molecules of xylose. According to Voss, the difficultly soluble xylan is accompanied by 20-25% of a uronic acid. The easily

soluble xylan was more easily split by fermentation than was the difficultly soluble one. K. Hess and M. Lüdtke (182) investigated the xylans from spruce sulfite pulp and from bamboo, and found them not to be identical.

It has already been emphasized that E. Schmidt and his co-workers isolated two xylans from wood, an easily soluble one, and a difficultly soluble one. E. Husemann (183) also extracted two xylans from beech wood xylan A, and xylan B. Xylan A was obtained by shaking 200 g. beech sawdust for two days with 3 liters of 8 % sodium hydroxide, after a pre-treatment under nitrogen with water and 0.2 % sodium hydroxide. The xylan was precipitated from the alkaline solution with methanol, treated for 1 day with 2 % chlorine dioxide solution, and washed with methanol and water. A white powder was obtained by reprecipitation from 6 % sodium hydroxide. $[x]_D = 87$ (in 6 % sodium hydroxide), CH_3O content = 0.85 %. Xylan B was obtained by acidifying the residue from the alkali extraction with acetic acid, washing, adding 50 liters of a 0.25 % ClO_2 solution and 500 cc. of pyridine, and shaking in the dark for 4 weeks. The material was washed in running water for 2 days, and extracted 2 days with 8 % sodium hydroxide. The xylan was precipitated from the extract with methanol, treated again with chlorine dioxide, and reprecipitated from sodium hydroxide. $[x]_D = 83$ (in 6 % sodium hydroxide).

The degree of polymerization of xylan A (measured osmotically) was 150; that of xylan B, was 157. These values are in good agreement with those obtained by osmotic measurements of benzylacetylxylan.

The question of the interpretation of the integral relationships between the quantities of cellulose, xylan, acetyl, and carboxyl groups has been the subject of much discussion.

M. Lüdtke (184) found that the parenchymatous cells of beech wood and bamboo shoots had higher xylan contents than the fiber tracheids. They also contain more solid carboxylic acids, and show a greater loss of material on fractionation with sodium hydroxide. Extraction with 0.2 % sodium hydroxide gives a residue which can by no means be considered to be a single chemical substance. The cellulose to xylan ratio of 3 : 1 is not stoichiometric. E. Schmidt's assumption that ester formation occurs is not tenable.

The results of E. Schmidt, which have been summarized above, require the assumption that a clear-cut separation of the constituents of the wood polyoses of hardwoods can be effected with alkali: the chief requirement is that the polyuronides should be completely removed.

I. A. Preece (185) has attempted to fractionate the soluble constituents of beech wood by the procedure of F. W. Norris and I. A. Preece (186).

The material was extracted first with ammonium oxalate, to remove the pectin, and then treated with a water-and-alcohol solution of sodium hydroxide, to remove soluble lignin constituents. Finally, the residue was extracted with hot 4% sodium hydroxide, which dissolved the "hemicellulose." The latter was precipitated with acetic acid, giving hemicellulose A. Fractional precipitation of the filtrate with acetone gave two more hemicelluloses. All three precipitates yielded xylose and uronic acids on hydrolysis; this indicates that a sharp separation of the various constituents can not be achieved, at least by this procedure.

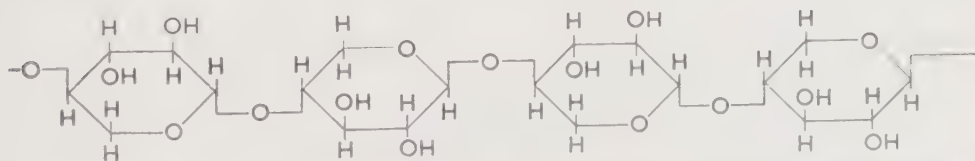
W. Voss, R. Bauer, and J. Pfirschke (487) confirmed the integral relationship between the quantities of xylan and of cellulose; they do not interpret this as being due to the presence of ester linkages (as E. Schmidt does), but believe that the coupling of xylan and cellulose is due to the morphological structure and to the fact that both of these components of the wood are end products of the same reaction (488):



According to these authors the strands of cellulose chains are surrounded by thin layers of pentosan chains. It is also often taken for granted that chemical combination occurs between the cellulose and the wood polyose chains (489). The firm combination between cellulose and certain wood polyoses, particularly pentosans has also given rise to the presumption that at the surface of the cellulose crystallites there may occur mixed crystallization of cellulose and the wood polyoses or lignin (490). According to this point of view there would be polar linkages between the cellulose and non-cellulose constituents. The possibility of various sorts of cross linkages has also been considered (491).

R. E. Dörr (492) believes that complete solution of the pentosans from straw is not practicable, since the pentosans are very intimately connected with the cellulose, and only a part of the compound can be separated without attacking the cellulose.

The structure of xylan has been elucidated by H. A. Hampton, W. N. Haworth, and E. L. Hirst (493). The method employed was the same as that used in determining the constitution of cellulose. It was found that xylan consist of β -xylopyranose residues, joined together in the 1 and 4 positions (494):



A comparison of this formula with that of cellulose immediately reveals

the similarity; the CH_2OH groups of cellulose have been replaced by hydrogen atoms. Haworth believes that these groups are lost by oxidative degradation of cellulose, with the formation of carbon dioxide.

The quantity of carbon dioxide given off when xylan from beech wood was treated with hot hydrochloric acid led E. Schmidt and co-workers (495) to conclude that this xylan consists of 16 xylose residues. This would mean that there would be one carboxyl group to 16 links in the chain. Later investigations have shown that no carboxyl groups are present in pure xylan. Schmidt's findings may be due to the presence in his xylan of polyuronic acids, which do occur in beech wood.

W. N. Haworth and his co-workers (496) found that esparto grass xylan, from which the arabinose component had been removed, gave 2,3-dimethyl-methylxyloside as the chief product when it was methylated and hydrolyzed, but that 7 % of trimethyl-methylxylopyranoside and an equal quantity of 2-methyl-methylxyloside were also formed. It was concluded that the arabinose component is attached to the end of a xylan chain which consists of 17 or 18 xylose units. The presence of 2-methylxylose indicates that several chains are connected together, as in the case of starch (497). E. Husemann's (498) investigations of the viscosimetry of xylans from beech and straw gave K_m values which were the same as those for cellulose; from this it was concluded that xylan consists of linear chains. This result can be reconciled with that of Haworth if it is assumed that the side chains are quite short, and do not influence the observed chain length.

Haworth estimated that the undegraded xylan in esparto grass contained about 90 pentose units. Husemann reports a degree of polymerization of 150 for xylans from straw and beech.

As far as the polydisperse nature of xylan is concerned, E. Husemann (498) found that approximately 95 % of all xylan of beech and straw consisted of chains of the same length. This uniformity is extremely remarkable.

2. Arabin. Arabinose is easily removed from the wood by very mild acid hydrolysis. L. Stockman and E. Hägglund (477) found that the "arabans" of spruce were quantitatively hydrolyzed by water at 120°C , yielding 0.7 to 0.8 % arabinose based on the original wood. L. E. Wise and R. C. Rittenhouse (498 a) proved the presence of arabinose in extracts obtained by heating three different pine woods with 0.01 N sulfuric acid. Spruce sulfite pulp did not yield any arabinose on acid hydrolysis, since this sugar had already been removed during the sulfite cook. On the other hand, a commercial kraft pulp yielded small amounts of arabinose.

H. Erdtman (498 b) has shown that arabinose, probably in the free state, is present in the heartwood of various pines, from which it can be extracted with acetone or alcohol. Similarly, arabinose has been isolated from the heartwood of *Thuja plicata* (498 c).

For the isolation of arabinose from beech and spruce and its occurrence in the form of arabogalactans see p. 138 and p. 151.

The method for the *quantitative determination of pentosan and pentoses* was for a long time quite defective. It was based on the work of Tollens, who found that furfural was formed on heating pentose-containing material with hydrochloric acid of a definite strength, and could be precipitated with phloroglucinol. Determination of pentosan in vegetable matter by the method of Tollens leads to quite inaccurate and widely-scattered results, since not only the pentosans, but also the accompanying carbohydrates, as well as the lignin, give volatile aldehydes, such as methylfurfural, hydroxymethylfurfural, and formaldehyde, which also are precipitated by phloroglucinol (499). It has also been found that the rate of distillation and the concentration of the hydrochloric acid must be carefully controlled if reproducible results are to be obtained.

C. Kullgren and H. Tydén (500) make use of a device of E. Öman (501) for maintaining the concentration of HCl. This consists in saturating the solution with sodium chloride.

A solution of 12 % HCl saturated with sodium chloride is also used by E. F. Hughes and S. F. Acree (502). In the procedure recommended by these authors, the furfural formed is driven off by steam distillation, which prevents decomposition of furfural and gives a practically theoretical yield of furfural from xylose. In the usual Tollens distillation the furfural yield amounts to only 88 % of the calculated value.

Various methods can be used for determining the furfural (503). A titrimetric bromide-bromate method is often employed (504). When pentosan in vegetable matter is determined by Tollens distillation, methylfurfural and hydroxymethylfurfural, which also consume bromine, are also formed; a correction must therefore be applied. Kullgren and Tydén propose redistilling the product; this destroys the hydroxymethylfurfural, but it is simpler to use *barbituric acid* as a precipitant, since it brings down only the furfural (505). With the barbituric acid precipitation it is necessary to apply a correction for the formaldehyde which may be formed in the presence of lignin (506). This correction is usually so small that it may be neglected (507). R. Lechner (508) asserts that the gravimetric determination of pentosan is to be preferred to the bromine titration if great accuracy is required.

Colorimetric methods for the determination of furfural have also been proposed. As aniline reacts with furfural, giving a red color, while the color produced with hydroxymethylfurfural is yellow and formaldehyde does not give any color at all, furfural can be determined colorimetrically without interference by the other aldehydes (509). However, the color obtained by aniline is not stable, and the same is true for the color produced by the action of orceine on furfural (510). By a modification of the orceine method recently worked out by A. Johansson (511), this disadvantage has been eliminated and a more convenient colorimetric method, specific for pentosan, has thus been developed.

G. Jayme and P. Sarten (512) report that 23.1 % hydrobromic acid has certain advantages over 13 % hydrochloric acid, in that no hydroxymethylfurfural is formed from hexoses during the distillation and the furfural yield is quantitative, which is not the case in the usual Tollens distillation. The furfural can be titrated with bromide-bromate, or precipitated with barbituric acid, or, if only small amounts of pentosan are present, thiobarbituric acid can be used to advantage.

3. Mannan. Mannose has been found among the products of acid hydrolysis of all the coniferous wood which thus far has been investigated. Hardwoods contain much smaller amounts of mannan, and frequently, none at all. G. Bertrand (513) and B. Tollens (514) were the first to establish the presence of mannan. The former found that the occurrence of mannan contents of gymnosperms were characteristic, and gave the following figures:

Kind of Wood	Mannose %
<i>Abies pectinata</i>	9.6
<i>Araucaria brasiliiana</i>	9.5
<i>Cupressus torulosa</i>	3.4
<i>Pinus laricio</i>	8.4
<i>Taxus baccata</i>	9.1

The mannan occurring in spruce wood was isolated and investigated by K. Hess and M. Lüdtkke (515), who extracted a sulfite pulp with 8 % sodium hydroxide. The mixture of xylan, cellulose, and mannan thus obtained was precipitated with acetic acid or alcohol, dissolved in cuprammonium solution, and a copper-alkali mannan precipitated by addition of sodium hydroxide. The mannan compound was further purified. The mannan thus obtained was identical with the mannan A of ivory nuts, for the rotation in 1N sodium hydroxide checked (mannan A: $(\alpha)_{17}^{17}$ 44.94°, mannan from pulp: $(\alpha)_{17}^{18}$ 44.58°), as did that in cuprammonium solution, and the X-ray diagrams (516).

In the case of mannan, too, there are evidently easily hydrolyzable and difficultly hydrolyzable forms, at least in spruce wood (517).

E. Husemann (183) emphasizes that it is impossible to extract the mannan of spruce wood by treatment with alkali, since it is very firmly held. Only when the wood has been pre-treated with chlorine dioxide is it possible to isolate mannan from the alkaline extract. This is done by fractional precipitation of the extract with methanol. The yield is not given.

The $(\alpha)_D$ value in sodium hydroxide, viscosity, and methoxyl content of each fraction were determined. The results are given in the following table.

Fraction	Amount g.	%	Cumulative Total %	η_{sp}/c (NaOH)	$(\alpha)_D$ in° (NaOH)	%CH ₃ O
I.....	0.62	6.2	6.2	0.066	— 20	0.92
II.....	0.47	4.7	10.9	0.066	— 25	0.85
III.....	1.18	11.8	22.7	0.072	— 42	0.68
IV.....	4.26	42.6	65.3	0.064	— 44	0.55
V.....	0.72	7.2	72.5	0.062	— 43	1.02
VI.....	1.34	13.4	85.9	0.065	— 44	2.24
VII.....	1.20	12.0	97.9	0.060	— 42	3.12
VIII.....	0.21	2.1	100.0	—	—	—
Before fractionation..	10.0	100.0	—	0.068	— 32	1.25

It will be seen from the table that about 90 % of the alkali-soluble material consist of fractions having rotations between — 42 and — 44 ; this is in agreement with the data of Hess and Lüdtke.

It also turned out that the individual fractions had quite different solubilities; Fractions V, VI, and VII dissolved easily in cold water and calcium chloride, while the other fractions were completely soluble only in sodium hydroxide and Schweizer's reagent. Husemann thought that these differences were attributable to differences in the methoxyl content.

Fractions V, VI, and VII were used to determine the degree of polymerization. Osmotic and viscosimetric measurements of mannan in CaCl₂ solution gave an average degree of polymerization of 160, while benzene solutions of acetylmannan gave 147. The K_m values were definitely lower than those found for cellulose, and varied considerably; Husemann nevertheless asserts that the data show that spruce mannan consists of stretched-out chains which are all approximately equal in length.

A. W. Schorger (518) has given a procedure for the *determination of mannan* in wood. Ten grams of fine sawdust was cooked for 3½ hours with 150 cc. of hydrochloric acid (d. 1.025). The mannose in the hydrolyzate was precipitated as the phenylhydrazone. Schorger thought that he had in this way converted all the mannan to mannose, but the following experiment of E. Hägglund and F. W. Klingstedt (519) shows that this is not the case:

Spruce sawdust, extracted with ether and acetone, was analysed for mannan according to Schorger's procedure, and 8.56 % of mannan was found. The residue after the hydrolysis was completely saccharified with 72 % sulfuric acid, and the mannose in the sugar determined by the method of Hägglund and Klingstedt. In two experiments where the mannose was precipitated directly, 2.9 % and 3.3 % of mannose were found; in two other cases a definite amount of pure mannose was added before precipitation, and the corresponding amount subtracted from the weight of the hydrazone, giving 3.19 % and 2.87 % of mannose. It is evident that the residues contain mannan which is difficultly hydrolyzable by the dilute hydrochloric acid used in Schorger's procedure; the latter method, therefore, yields only qualitative results.

This procedure has nevertheless been used for the determination of the distribution of mannan between the Cross-Bevan cellulose and the remainder of the wood in various kinds of wood (520). [The Cross-Bevan cellulose was determined by a modification of the method of A. G. Norman and S. H. Jenkins (521)]. The results can not claim any great accuracy, but it was definitely apparent that by far the larger quantity of the mannan of many softwoods is intimately associated with the cellulose.

The following method, due to E. Hägglund (522) and his co-workers, can be recommended for the quantitative determination of mannan:

Five g. of air-dried material (sawdust or pulp) which has been extracted with acetone for 6 hours in a Soxhlet, is treated at room temperature with 45 cc. of 72 % sulfuric acid (d. 1.64). [H. Koch (523) recommends using as low a temperature as possible, even going down to -10°C . in order to avoid a transformation of the mannose. It is doubtful, however, if any significant reaction occurs when the saccharification is limited to a few hours, and when the starting material is mannan rather than mannose.] The mixture is stirred with a glass rod, the beaker is placed in a desiccator and the dissolved air is removed by evacuating two or three times. This is necessary in the analysis of pulp, but not absolutely so when wood is being examined. After 4 hours the solution is diluted with 95 cc. of water, and allowed to stand 6 hours or more at room temperature. The solution is transferred to a 2-liter flask, diluted with 1,500 cc. of water, and refluxed for 6 hours. The lignin which precipitates out can be filtered off only rather slowly. However, it is not necessary to remove all the lignin; it is more advantageous to take a small sample of the solution and determine its sugar content. The total sugar can then be calculated from the total volume of the solution. The solution is neutralized with barium carbonate in a porcelain dish while it is

warm, the carbonate being stirred up to a paste with water, and added gradually to the sugar solution. The barium sulfate and lignin are filtered off simultaneously on a Buchner funnel, after the solution has cooled. This filtration proceeds quite easily. Since a thorough washing of the residue entails a great dilution of the solution, one takes 1,000 cc. of the filtrate, for example, and determines the sugar in it; since the total sugar content has previously been determined, one can tell what fraction of the solution this is. The solution is now concentrated in a porcelain dish on a water bath; when the volume reaches 200-300 cc. the solution is quantitatively transferred to a pyrex dish, and concentrated to 75 cc. on the water bath. The acidity of the solution must be carefully controlled. The use of excess barium carbonate makes the solution slightly alkaline; in this case the solution should be made slightly acid with acetic acid. The reaction of the solution must be controlled during the concentration, too. It should be acid to litmus, but not to congo. A part of the solution adheres to the edge of the dish during the concentration, and may be decomposed, with the formation of a brown discoloration; this may be avoided by rinsing with water. The time required for the concentration is about 4—5 hours. After being concentrated, the solution is filtered and transferred quantitatively to a 100 cc. glass-stoppered Erlenmeyer flask, in which the mannose can be determined. (This procedure yields a quantity of sugar corresponding to a 107-109 % yield of glucose from wood, and 109-112 % from pulp. Pure cellulose gives 111 % of glucose; it may be concluded, therefore, that the saccharification is practically quantitative, that no significant amount of sugar is lost during the concentration, and that no humus formation from carbohydrate occurs during the saccharification.)

The mannose in the hydrolyzate is determined as follows: A knife's-point of sodium acetate is added to the filtrate in order to neutralize any possible traces of mineral acid. About 0.5 g. of pure mannose, weighed with an accuracy of 1 mg., is added to the solution, and a quantity of phenylhydrazine equivalent to the total sugar present in the solution is added (the phenylhydrazine is dissolved in 1.6 times its weight of 25 % acetic acid.) The Erlenmeyer is now filled with distilled water, and closed with the glass stopper. After 15-20 hours at room temperature the hydrazone is filtered off on a glass filter, washed three times with 5 cc. portions of ice water, twice with 5 cc. portions of absolute alcohol, and then twice with 5 cc. portions of ether. The hydrazone can be dried for 4 hours at 95° C.

The mannan content of various materials was determined by this method. (For spruce wood the analysis was also made by Schorger's method, which has been remarked to give low values.)

Per cent of Mannan

Substance	Method	
	Hägglund-Proffe	Schorger
Spruce wood.....	10.5	8.0
Sulfite pulp, unbleached pre-extracted	7.3	—
Sulfate pulp.....	6.0	—
Pulp for artificial silk, pre-extracted	5.7	—
Viscose rayon.....	1.0	—

The following values reported by Schorger are of interest. It should be remembered that he determined only the relatively *easily-hydrolyzable mannan*.

Gymnosperms

Kind of Wood	%	Kind of Wood	%
Douglas fir (<i>Pseudotsuga taxifolia</i>)	6.65	Sugar pine (<i>P. Lambertiana</i>)....	4.67
Corkbark fir (<i>Abies arizonica</i>)...	6.57	Coulter pine (<i>P. coulteri</i>)	
Western larch (<i>Larix occidentalis</i>)..	5.13	A. heartwood.....	5.40
Arbor vitae (<i>Thuja occidentalis</i>)..	1.44	B. sapwood.....	6.28
White spruce (<i>Picea canadensis</i>)..	7.12	Monterey Pine (<i>P. radiata</i>).....	7.68
Longleaf pine (<i>Pinus palustris</i>)...	4.75*	Pinon pine (<i>P. edulis</i>).....	6.00
Loblolly pine (<i>Pinus taeda</i>).....	5.10	Western white pine (<i>P. monticola</i>)	
Whitebark pine (<i>P. albicaulis</i>)....	4.22	A. heartwood.....	7.13
Western yellow pine (<i>P. ponderosa</i>		B. sapwood.....	7.44
<i>scopelorum</i>).....	4.64	Digger pine (<i>P. sabiniana</i>).....	7.17
Jeffrey pine (<i>P. jeffreyi</i>).....	5.40	Limber pine (<i>P. flexilis</i>).....	5.94
Cuban pine (<i>P. heterophylla</i>)		Bristlecone pine (<i>P. aristata</i>)....	5.41
A. heartwood.....	5.81		
B. sapwood.....	9.22		

* Only 1.64 % of mannan was found in another sample.

Six different hardwoods were also analyzed for mannan; they were basswood (*Tilia americana*), sugar maple (*Acer saccharum*), yellow birch (*Betula lutea*), green ash (*Fraxinus lanceolata*), white ash (*F. americana*), aspen (*Populus tremuloides*). No mannan could be detected in any case.

These figures of Schorger's may be supplemented by those of W. H. Dore (524), who followed exactly the same procedure as Schorger, and obtained the following values:

Percent of Mannan in Sapwood

Redwood (<i>Sequoia sempervirens</i>)	3.21
Yellow pine (<i>Pinus ponderosa</i>)..	6.37
Sugar pine (<i>Pinus lambertiana</i>)..	6.63

4. Glucan. Recent investigations of E. Hägglund and L. Stockman (477), as well as of B. Hägglund (525), have shown that the spruce wood polyoses which are hydrolyzable by faintly acid buffer solutions contain only very small amounts of glucose, if any. It was found that 10.1 % of the wood went into solution in 18 hours at 120° C. on treatment with a buffer of pH 4. The carbohydrates going into solution consisted chiefly of

oligosaccharides, since the reductive power of the solution could be tripled or quadrupled by further hydrolysis (526). Only 75 % of the organic matter in the solution could be obtained in the form of simple sugars by complete hydrolysis. The mixture of monosaccharides thus obtained consists, as may be seen from the table below, chiefly of mannose, xylose, and galactose.

A further 11.2 % of the wood (based on the original weight) went into solution on subsequent treatment for 24 hours at 120 °C with a solution of pH 2. The carbohydrates in this solution, which constituted 73 % of all the dissolved organic materials, were almost entirely monosaccharides; the reductive power could be increased only insignificantly by further hydrolysis. The composition of this sugar mixture is also given in the table.

The residue from these two hydrolyses was finally treated for 24 hours at 120 °C with a solution of pH 1; this caused another 7.6 % of organic materials (on the basis of the original weight) to go into solution. The organic matter dissolved in the last treatment contained 79 % of monosaccharides; the composition of this fraction is also given below.

Percentage Composition of Hydrolyzate

Sugar	Obtained at		
	pH 4 %	pH 2 %	pH 1 %
Mannose	40.2	47.5	31.4
Galactose	13.8	14.6	—
"Xylose"	33.6	22.1	21.9
"Glucose"	4.8	2.0	45.1
Undetermined . .	7.6	13.8	1.6

Arabinose could be shown to be present only in the hydrolyzate obtained at pH 4. One third of the "xylose" obtained at that pH (see table) actually consisted of arabinose. The amount of arabinose was 0.8 % of the total wood.

The galactose has been determined as mucic acid (527), and the xylose as furfural after distillation with hydrochloric acid (528). Glucose is calculated as the difference between the total sugar fermentable with baker's yeast and the mannose determined as the phenylhydrazone (529). An attempt was made to determine the glucose as phenylglucosazone in the filtrate from the mannose phenylhydrazone; this was successful only in the solution obtained at pH 1.

It is evident that the most easily hydrolyzable portion of the wood polyoses contains very little glucose, if indeed it contains any at all. The carbohydrates which yield galactose were, as was to be expected, the most easily hydrolyzed (530).

It is not clear whether the glucose which is dissolved out at pH 1 comes from a difficultly-hydrolyzable polysaccharide which contains glucose, or whether it is formed by degradation of the cellulose in the amorphous regions.

The following total quantities of sugar (based on the weight of the wood) were dissolved out:

	pH 4	pH 2	pH 1	Total
Sugar dissolved (% of weight of the wood)....	7.6	8.3	6.0	21.9

These results agree quite well with those of another study carried out quite a long time ago in the author's institute. In this case 101.7 g. of wood was heated to 135° C. for 4 hours with 875 cc. of 0.5 % sulfuric acid, and a yield of sugar equal to 20.6 % of the weight of the wood was obtained. The composition of this sugar mixture was as follows:

	%
Mannose.....	41.0
Glucose.....	34.2
Xylose.....	19.7
Galactose.....	5.1

In view of the fact that the hydrolysis was carried out under different conditions, the agreement with the results of the previously mentioned experiment is remarkable.

K. Hess, M. Lüdtke, and H. Rein (531) investigated the carbohydrate in young beech shoots. They extracted the wood with 5 % or 8 % sodium hydroxide and fractionated the extract by precipitation from Schweizer's solution. Alkali-soluble cellulose was not present, but a glucosan was claimed to be present in the xylan fraction. This carbohydrate was not further investigated.

B. Hägglund and L. Stockman (unpublished experiments), at the author's institute, have tried to prepare a glucan from spruce wood by a similar procedure. These attempts were, however, without success.

An observation made by G. Jayme and G. Hanke, and by G. Jayme and F. Fink (532) should be mentioned in this connection. These authors digested spruce with sodium chlorite, obtaining the "theoretical" yield of polyoses in the holocellulose. Upon hydrolysis of the remaining solution 2.9-3.7 % of glucose (caled. on wood) was found, indicating the presence of a polysaccharide which might constitute one of the components of the native lignin ("protolignin"). It appears more probable, however, that polysaccharides coming from the carbohydrate part of the wood and containing glucose go into solution during the preparation of the holocellulose. The authors also suggest this possibility. It seems quite probable that these polysaccharides become water soluble because of the removal of the lignin.

O. Müller (533) recently reported that a polysaccharide, probably of the hexosan type, is extracted by treatment of beech wood with sodium chlorite. The author assumes, that this substance, which contains methoxyl groups, is a "lignin fragment."

5. Galactan. Small amounts of galactose were recognized at an early date among the sugars of sulfite waste liquor (534). The figures quoted are quite divergent; while H. Krause found only traces of galactose, P. Klason and E. Hägglund reported a galactose content equal to 0.27-1.3 % of the weight of the wood.

E. Hägglund and F. W. Klingstedt (535) found no carbohydrates which yield galactose in sulfite pulp from spruce; it must therefore be assumed that the galactan which occurs in small quantities in spruce wood is easily and completely dissolved by hydrolysis of the wood. This is in accord with the results of A. W. Schorger and D. F. Smith (536). It should be noted, however, that isolation of cellulose by the Cross-Bevan procedure does not completely remove the galactan (537). When spruce cellulose prepared in this way was saccharified with 72 % sulfuric acid, the sugars were found to contain 1 % of galactose, corresponding to 0.55 % of the weight of the wood. Since the total quantity of galactose originally present was 1.4 % of the weight of the wood, 40 % of the galactan remained undissolved by the Cross-Bevan procedure.

W. H. Dore (538) determined the galactan content by direct oxidation with acid, and obtained the following yields from several kinds of wood:

	Galactan
Redwood.....	0.50
Yellow pine.....	0.78
Sugar pine.....	0.50

Water-extraction of the larch (*Larix occidentalis*) by A. W. Schorger and D. F. Smith (536) yielded carbohydrates in quantities equal to no less than 8-17 % of the weight of the wood. By far the largest part consisted of galactan, which was called "ε-galactan." The carbohydrates were investigated by L. E. Wise and his co-workers (539) who found that they yielded *arabinose* and *galactose* on hydrolysis, in a molecular ratio of about 1 : 6. A carbohydrate of the same composition was also obtained from *Larix laricina* Koch and from Siberian larches. It was at first thought that a true pentosanhexosan was present, rather than a mixture of araban and galactan. E. Husemann (483) attempted to confirm this by fractional precipitation with methanol and examination of the individual fractions with respect to their optical rotations, degree of polymerization, etc. This attempt was unsuccessful, however, because the fractions showed

great similarities to each other. L. E. Wise and his co-workers (540) have found that fractionation of the acetyl, propionyl, and benzoyl esters yields no uniform derivatives; they conclude, therefore, that arabo-galactan is itself a mixture. The investigations of E. L. Hirst, J. K. N. Jones, and W. G. Campbell (541) support this conclusion.

The thorough investigations of E. V. White (542) have shown, however, that the carbohydrate consists of a uniform polysaccharide, in which six galactose residues and one arabinose residue really are joined. The galactose units are not joined together in a chain; the molecule is probably highly branched.

The presence of galactan in hardwoods has also been demonstrated. J. König and E. Becker (543) obtained 3.5 % of galactose from birch and 0.1 % from beech by hydrolysis with dilute sulfuric acid under pressure.

E. Schmidt, M. Atterer and H. Schnegg (544) investigated the skeletal substance of spruce, esparto, beech, flax, hemp, and rye, and found that no galactan was present. The procedure for preparing the skeletal substance would not have caused galactans to go into solution; hence it was concluded that these woods and grasses contain no galactan. The galactose in the hydrolyzate was determined by fermenting the sugar with yeasts which ferment galactose and with those which do not. The galactose could be determined by difference; as has been said, none was found to be present.

E. F. Kurth and G. J. Ritter, who investigated the easily hydrolyzed part of the holocellulose from American spruce, came to a different conclusion. They obtained the following results (545):

Components of the Easily Hydrolyzed Wood Polyoses in Spruce Holocellulose

Component	% of the Material Examined	% of the Wood
Mannan	17.7	1.8
Glucan	8.0	0.8
Galactan	7.8	0.8
Araban	12.5	1.3
Xylan	20.9	2.2
Methoxyl	3.2	0.3
Glucuronic acid	14.6	1.5
Volatile acids, acetyl and formyl groups	8.0	0.8
Undetermined	7.3	0.8
Total	100.0	10.3

The galactan was determined by oxidation to mucic acid, and also by selective fermentation with *Torula dattila* and *Saccharomyces cerevisiae*. The latter ferments galactose, while the former does not. It therefore seems to be conclusively proved that galactan is present in certain types of wood.

A polysaccharide containing 72.6 % galactose, which was determined by the biochemical method of L. E. Wise and J. W. Appling (546), has been isolated by F. E. Brauns (547) from *Picea mariana*.

L. Stockman and E. Hågglund (477) came to the result that Swedish spruce contains 1.8 % galactan.

6. Fructan. The presence of small amounts of fructose in hydrolyzates prepared from sulfite pulp with strong sulfuric acid has been demonstrated by the specific color reactions (439) as well as by the isolation of fructose-methylphenylhydrazone, melting at 147-148°C (535).

Other authors (548) did not find any fructose on partial hydrolysis of white spruce with dilute mineral acids.

Similar results have been reported regarding sulfite waste liquors. In rayon pulp waste liquors, which have been prepared under relatively strongly hydrolytic conditions, J. Sundman (548 a) found small amounts of fructose to be present. In strong pulp waste liquors no fructose had been detected.

From these data it appeared as if a fructan belonging to the difficultly-hydrolyzable polyoses might be present in wood.

Recently, J. Sundman (548 b) pointed out that, under the experimental conditions previously used, fructose may have been formed from glucose or mannose by epimerization. Carefully controlled total hydrolysis, which practically precluded both the destruction of fructose and its formation from other sugars, showed that no fructan was present in spruce, pine, or birch. Holocellulose, as well as rayon and paper pulps made from spruce, were also found to be free from fructan.

7. Pectin. In this connection it may be well to discuss the occurrence of pectin in wood.

Pectin is a substance which is very widely distributed in plant tissues. In its native form it is called by various names, such as protopectin, primary pectin, and true pectin. It is insoluble in cold water, but is dissolved by heating with boiling water or with very dilute acids, and may be precipitated from the solution with alcohol. The "hydratopectin" which is isolated with boiling water was first studied extensively by F. Ehrlich (549), who reported that it was composed of 70-80 % of the calcium and magnesium salts of "pectic acid," and of 20-30 % of araban which was bound coordinately. Ehrlich stated that the pectic acid had a complicated ring structure in which galacturonic acid, galactose, arabinose, acetyl groups, and methoxyl groups were present. He also elaborated certain hypotheses as to the structure of the native pectin, but these are no longer of interest.

The pectins are now considered to be compounds of high molecular weight. They consist of chains of galacturonic acid residues, partly esterified with methyl alcohol, partly in the form of salts with polyvalent cations like calcium and magnesium, and are also combined with araban and galactan. The carboxyl groups bound to the polyvalent ions may belong to the same molecule, or they may belong to different molecules, giving rise to cross linkage. F. H. Henglein (550) believes that it is also possible that polymeric carbohydrates like araban, which contain a certain number of carboxyl groups, may also be cross-linked with the polygalacturonic acid chains.

T. v. Fellenberg had earlier found that pectin is easily hydrolyzed with alkali, and that methyl alcohol is formed during this process (551). On the basis of this property, he attempted to decide whether or not pectins existed in wood. He subjected fir wood which had been completely extracted with water, alcohol, and ether to the action of dilute sodium hydroxide, and found that only 0.05 per cent of methyl alcohol was split off. This fraction might be termed "pectin methyl alcohol," but the presence of pectic acid could not be demonstrated. Dilute acid at 120° C did not dissolve pectin from the wood either. It has nevertheless been assumed by various authors that wood does contain a wood pectin. It is, however, not certain that the methyl alcohol which is easily split off by alkali must necessarily be derived from pectin. The quantities of methyl alcohol which are obtained from various woods in this manner are quite small, as the following figures indicate (552):

Kind of Wood	% of the Weight of the Wood	
	Methyl Alcohol, Obtained by v. Fellen- berg's Method	Pectin, Calculated as Methyl Alcohol $\times 10$
Spruce.....	0.122	1.22
Pine.....	0.111	1.11
Beech.....	0.175	1.75
Birch.....	0.161	1.61
Poplar.....	0.182	1.82

Older reports, which have been confirmed by M. M. Mehta (553) state that the middle lamella in the wood of young twigs and stems contains pectin, while older wood is lacking in pectin. F. Ehrlich (549) assumes that the pectin changes into lignin-like compounds as the wood grows older.

G. J. Ritter (554) attempted to isolate the pectin from various American woods (basswood, red alder, and pine) by extraction with dilute ammonium oxalate, but he was not successful. On the other hand, it has been found that most of the lignified woods give various uronic acids on hydrolysis. E. Hägglund, F. W. Klingstedt, T. Rosenquist, and H. Urban (555) for example, were able to demonstrate the presence of galacturonic acid in

the sulfite waste liquor from spruce. C. G. Schwalbe and G. A. Feldtmann (556) found glucuronic acid in straw, and M. H. O'Dwyer had earlier isolated a substance very similar to pectin by treating beech with ammonium oxalate (557). Later, she also succeeded in demonstrating the presence of glucuronic and galacturonic acids along with xylose, arabinose, and galactose, when beech wood was hydrolyzed with strong acid (558).

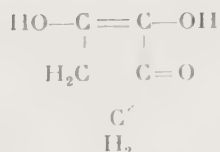
The substance obtained by alkaline extraction of beech was separated into two fractions, A, and B. O'Dwyer obtained fraction A by precipitation with acetic acid, while B was obtained from the filtrate from the precipitation of A, by a second precipitation with alcohol. Hydrolysis with 12 % hydrochloric acid yielded carbon dioxide; fraction A gave an amount corresponding to 11 % of uronic acids, and B, an amount corresponding to 63 %. Glucuronic acid could be shown to be present in A, while B contained galacturonic acid. Further investigations of the uronic acids in wood were published later (559).

M. H. O'Dwyer (560) later investigated the fraction A more intensively, using material from both the heartwood and the sapwood of oak. The smallest unit from the heartwood consisted of 11 xylose residues and 1 methylhexuronic acid residue, while that from sapwood consisted of 11 xylose residues, 1 glucose residue, and 1 methylhexuronic acid residue.

S. C. Rogers, R. L. Mitchell, and G. J. Ritter (561) extracted maple wood first with 20 % and then with 3 % potassium hydroxide at 65-70° C. The dissolved material, amounting to 14 % of the weight of the wood, contained 75-80 % pentosans and at least 15 % uronic acids, which is more than twice the amount previously obtained by O'Dwyer.

O. Wurz (562) believed, remarkably enough, that pectin is present in sulfite pulp; this was indicated only by the color reaction with ruthenium red.

From hydrolyzates, obtained by pressure heating of beech wood with water or oxalic acid solution at 100-150° C, small amounts of reductinic acid



have been isolated by A. W. Sohn (562 a). The same substance, which is closely related to ascorbic acid and has strong reducing properties, has been detected in corresponding extracts from spruce and pine wood. The above author has discussed the possible formation of this substance from a 2-ketohexonic acid (562 b), which may be present in beech wood extracts.

or from other wood constituents, such as pentoses. There is also a possibility that the substance exists as such in wood.

3. The Occurrence of Polyoses in Different Woods, their Dissolution and Determination. H. Krause (563), E. Hägglund (564), P. Klasen (565), and T. Höpner (566) have investigated the sugars of sulfite waste liquor and found that they contained pentoses and mannose as important constituents.

The presence of glucose in varying quantities has also been reported by these authors, but a recent check of the glucose content of sulfite waste liquors has shown that it is certainly very much lower than was previously thought. L. Stockman and E. Hägglund (477), for example found the percentage composition of the sugar in various sulfite waste liquors to be as follows:

	%
Mannose.....	45-50
Galactose.....	15-20
Xylose.....	22-26
"Glucose".....	5-10

The glucose was determined (as in earlier work) as the difference between total fermentable sugar and the analytically determined sum of mannose plus galactose.

J. Sundman (548 a, 567) has attempted to determine the composition of the sugar in sulfite waste liquor by a new method, based upon the fact that the dissociation constants for the sugarbisulfite compounds have different values for each of the sugars. He finds by this method that the waste liquor from strong sulfite cooks contains no glucose at all. On the other hand, in the waste liquor from the preparation of rayon pulps which is carried out at low pH and with a high final temperature, 5-15 % of the total hexose proved to be glucose. The values obtained by Sundman for the composition of the sugars in various sulfite waste liquors are given in the following table (in % of the total hexose):

Composition of the Hexose in Sulfite Waste Liquors

Liquor	Roe Chlorine No. of the Pulp	% of the Total Hexose		
		Mannose	Galactose	Glucose
1.....	8.3	87	13	0
2.....	5.6	88	12	0
3.....	strong pulp	89	11	0
4.....	strong pulp	90	10	0
5.....	4.4	88	7	5
6.....	1.6	91	Traces	9
7.....	1.5	85	Traces	15
8 (Sulfite pulping of pine)	7.0	79	21	0
9 (Magnesium bisulfite pulping).....	1.9	79	12	9

The low glucose content of the sulfite waste liquors is in good agreement with the observation mentioned above (p. 149) that only relatively small amounts of glucose go into solution when spruce wood is hydrolyzed with mild acid, at pH 2, for example. This result is also confirmed by the following unpublished experiment of L. Stockman and E. Hägglund, in which the easily hydrolyzable fraction of the wood polyoses was investigated. When spruce sawdust was heated for 24 hours at 120° C with 0.01 N sulfuric acid, 22.0 % of the wood was dissolved, and the sugar solution obtained, representing 16.0 % of the wood, had the following composition:

Mannose.....	46.0
Arabinose.....	0.5
Xylose.....	29.5
Galactose.....	11.0
"Glucose".....	4.0
Undetermined.....	9.0
	<hr/> 100.0

J. König and E. Becker (568) attempted to determine the wood polyose contents of various woods. The wood was hydrolyzed for 4-5 hours with 0.4 % sulfuric acid under a pressure of $1\frac{1}{2}$ - $3\frac{1}{2}$ atm. The following results were obtained.

Kind of Wood	Wood Polyoses According to König		
	Hexosans	Pentosans	Total
Fir I.....	13.58	8.67	22.25
Fir II.....	13.00	9.74	22.74
Pine.....	12.78	8.70	21.48
Birch I.....	4.61	23.20	27.81
Birch II.....	5.00	21.48	26.48
Poplar I.....	2.60	15.36	17.96
Poplar II.....	3.43	15.10	18.53
Beech.....	4.36	17.79	22.15
Oak.....	5.70	19.29	24.99
Willow.....	5.05	16.75	21.80
Alder.....	3.65	15.90	19.55

The percentage compositions of the sugars which went into solution were determined for some of the woods. The results were:

Sugar	Conifers		Hardwoods	
	Fir	Pine	Birch	Beech
Pentose (xylose).....	26.0	24.8	61.1	73.9
Glucose.....	23.4	21.4	24.4	20.1
Galactose.....	3.4	4.2	3.5	0.1
Mannose.....	24.6	43.4	7.1	3.3

The presence of fructose was not demonstrated.

E. C. Sherrard and W. G. Blanco (569) have also determined the yield and composition of the sugar obtained by a 15-minute hydrolysis of American spruce (white spruce) with dilute sulfuric acid at pressures of

7.2–7.8 atm. The yield varied between 20 and 27 %, depending on the concentration of the acid. The average composition of the sugar was as follows:

Mannose.....	37.7
Glucose.....	29.3
Galactose.....	6.4
Xylose.....	13.3
Arabinose.....	5.4
Volatile reducing substances....	7.9
	<hr/> 100.0

The sugars were determined by fermenting the mannose and glucose with yeast, and then treating the residue with a lactic acid bacterium which attacks galactose and arabinose, but not xylose.

These authors later attempted to isolate the wood polyoses themselves from spruce, and to investigate them further (570). It turned out that water-soluble polysaccharides could be derived from the residue obtained from the chlorination of wood according to the Cross-Bevan procedure. Up to 20 % of the pulp could thus be brought into solution. The extracted material was, remarkably enough, partly crystalline, but it did not appear to be uniform. It contained 20% of pentoses and 30% of mannose.

E. Hägglund (571) attempted unsuccessfully to obtain water-soluble polyoses from Finnish spruce by the method of Sherrard and Blanco.

It has already been emphasized that not all the wood carbohydrates which are grouped with the cellulose are easily dissolved during hydrolysis. Some of the carbohydrates are so firmly attached to the pulp that they have been justifiably designated as polysaccharides of the cellulose type (572). In spruce these polysaccharides were assumed to consist of mannan, xylan, and fructan (535). As already mentioned (p. 153), it has been shown, however, that no fructan is present in spruce.

The pentosan content of spruce has already been discussed. There has been some dispute as to whether this consists of xylan or araban, or a mixture of both. P. Klason's investigations (573) indicated that the pentosan of spruce consists exclusively of araban. This conclusion was based on the fact that the sulfite waste liquor, after treatment with α -naphthylamine sulfate to remove the lignosulfonic acid, gave a precipitate with *p*-bromophenylhydrazine which Klason thought was arabinose *p*-bromophenylhydrazone. E. Hägglund's investigations (574) show that this is really mannose *p*-bromophenylhydrazone. Indications were found that the hydrochloric acid lignin is accompanied by very small amounts of arabinose, amounting to less than 1 % of the weight of the wood (575). Later investigations of E. Hägglund (574) have shown that by far the larger portion of the pento-

sans in spruce must consist of xylan. E. F. Kurth and G. J. Ritter (545) have identified xylose in hydrolyzates from spruce holocellulose by the formation of the p-bromophenylhydrazone and the methylphenylhydrazone. The presence of xylose in hydrolyzates from spruce has also been shown by J. Sundman, J. Saarnio, and C. Gustafsson (575 a) who used a paper-chromatographic method.

The studies of B. Tollens and his co-workers (576) establish the fact that small amounts of araban are found along with the xylan.

It may also be mentioned that Sherrard and Blanco (570) found considerable quantities of araban along with the xylan in the wood of American spruce.

Kurth and Ritter (545) stated that approximately one-third of the pentosans of the holocellulose of American spruce consisted of araban. K. Freudenberg and co-workers (476) who have isolated xylose and arabinose from spruce hydrolyzates estimated the content of xylose in spruce wood to be about 5% and that of arabinose, 0.8-1.0%.

In the paper-chromatographic studies of Sundman, Saarnio, and Gustafsson (575 a) arabinose was shown to be present in the hydrolyzates of all softwoods examined, whereas it was lacking or present only in small amounts in the hydrolyzates of hardwoods.

Older figures on the *pentosan content of woods* are all inaccurate, as has been pointed out above (p. 143), since hydroxymethylfurfural is formed from the wood polyoses, and formaldehyde is split from the lignin during the determination. Both are precipitated with phloroglucinol during the furfural determination, and the results for pentosan are thus too high. The following figures of G. de Chalmot (577) for the pentosan content of a number of American woods are therefore not very accurate:

	% Pentosan
Birch (<i>Betula</i> sp.)	23.4
Beech (<i>Fagus ferruginea</i>)	21.0
Water oak (<i>Quercus nigra</i>)	21.3
White ash (<i>Fraxinus americana</i>)	17.5
White elm (<i>Ulmus americana</i>)	17.4
White pine (<i>Pinus strobus</i>)	7.4
Shortleaf pine (<i>Pinus mitis</i>)	8.8
Hemlock (<i>Tsuga canadensis</i>)	6.0

These figures may be supplemented by those of A. W. Schorger (578), S. A. Mahood and D. E. Cable (579), and G. J. Ritter and L. C. Fleck (580). It should be noted that these figures for pentosan are based on the alcohol-insoluble portion of the phloroglucinol precipitate. There is no guarantee, however, that only pentosans are thus determined, for as E. Hagglund and F. W. Klingstedt (519) have pointed out, the phloroglucinol compound of hydroxymethylfurfural is not very easily soluble in alcohol.

	% Pentosan
Yellow birch (<i>Betula lutea</i>)	24.6
Basswood (<i>Tilia americana</i>)	19.9
Eucalyptus (<i>Eucalyptus globulus</i>)	20.1
Tanbark oak (<i>Quercus densiflora</i>)	19.6
White spruce (<i>Picea canadensis</i>)	10.4
Western larch (<i>Larix occidentalis</i>)	10.8
Western yellow pine (<i>Pinus ponderosa</i>)	7.4
Longleaf pine (<i>Pinus palustris</i>)	7.5
Western white pine (<i>Pinus monticola</i>)	7.0
Douglas fir (<i>Pseudotsuga taxifolia</i>)	6.0

It will be seen from these figures (and it has already been pointed out in another connection) that the pentosan content of hardwoods is two to three times as great as that of conifers. The smaller the true pentosan content, the more uncertain are the values given above, because the percentage of hydroxymethylfurfural in the mixture with furfural is then higher.

G. J. Ritter and L. C. Fleck (581) investigated the pentosan content of heartwood and sapwood, using phloroglucinol as a precipitant. Great differences between the heartwood and sapwood were only exceptionally observed, as the following figures indicate:

	% Pentosan	
	Heartwood	Sapwood
Hemlock	9.06	8.79
Redwood	8.86	10.04
Red mulberry	20.28	21.16
Sugar maple	20.42	20.50
Red oak	20.95	21.88

E. Hägglund and his co-workers (582) have investigated the variation in the true pentosan content of wood taken from different parts of spruce trunks grown in various regions of Sweden; the following results may be quoted:

Spruce				
Characteristics of the Wood			Height on the Trunk	
Diameter of the Trunk, cm.	Specific Gravity	Number of Annual Rings per cm.	Below the Crown % Pentosan	Within the Crown % Pentosan
44	0.28	1.7	6.8	—
38	0.38	1.4	—	6.9
22	0.39	3.4	8.3	—
14	0.40	3.7	—	9.1
21	0.40	18.5	8.5	—
12	0.42	17.4	—	9.2

It is clearly evident that the pentosan content of the top wood is greater than that of the butt. This is also the case with pine wood, as may be seen from the following figures (583).

Pine

Characteristics of the Wood			Height on the Trunk	
Diameter of the Trunk, cm.	Specific Gravity	Number of Annual Rings per cm.	Below the Crown % Pentosan	Within the Crown % Pentosan
23.0	0.40	2.8	9.0	—
10.6	0.41	3.2	—	11.0
12.8	0.36	2.8	10.0	—
12.0	0.36	2.0	—	11.9
17.6	0.39	21.0	10.7	—
11.0	0.39	18.0	—	11.4

The pentosan content of the wood varies not only with the height on the trunk, but also from one annual ring to another at the same height, as the following figures indicate (584):

Pentosan Content (in %) of Spruce Wood

Sample	Trunk No. 1	Trunk No. 2	Trunk No. 3
Heartwood.....	8.58	7.90	8.86
Inner portion of sapwood....	8.63	8.02	8.87
Outer portion of sapwood...	9.17	8.04	9.41

E. Hägglund and T. Johnson (585) have determined the pentosan contents of spring- and summerwoods of spruce, with the following results:

	Springwood	Summerwood
Spruce (<i>Picea excelsa</i>	7.58 %	6.77 %

In this connection it is well to discuss the question as to whether or not the so-called *furfuroids* occur in wood. The term is due to C. F. Cross and E. J. Bevan (586), who thought that the furfural obtained in the Tollens distillation of wood did not come exclusively from the pentosan, but also from the *furfuroids*, which are naturally occurring oxycellulose. The cellulose of certain plants, like straw and esparto grass, was supposed to be particularly rich in *furfuroids* (587). This point of view has been hotly contested, but attempts to defend it have continued for a long time (588).

Several facts are in contradiction to the hypothesis of Cross and Bevan. E. Heuser and A. Haug, for example, demonstrated that the yield of furfural from straw cellulose, which according to Cross and Bevan amounts to about 12 % when the cellulose has a high copper number, can be reduced to a very small value by extracting the crude cellulose with alkali. The cellulose itself remains unchanged. The high yield of furfural is therefore due to the presence of xylan. It has also been shown that the furfural obtained by a Tollens distillation of esparto pulp is derived chiefly from the xylan of the pulp (589).

REFERENCES TO CHAPTER III. SECTIONS I. II. AND III
(pp. 37-161)

1. Gottlieb, E., *J. prakt. Chem.* [2] **28**, 392 (1883).
2. Daube, W., *Forstl. Blätter* **20**, 392 (1883).
3. Braconnot, H., *Ann. chim. et phys.* [2] **12**, 172 (1819).
4. Payen, A., *Compt. rend.* **7**, 1052 (1838).
5. Payen, A., *Compt. rend.* **8**, 51, 169 (1839); **10**, 941 (1840).
6. Schleiden, M. J., *Poggendorff's Ann.* **43**, 391 (1838); *Ann.* **42**, 298 (1842).
7. Erdmann, J., *Ann.* **138**, 1 (1866); *ibid.* Suppl. **5**, 223 (1867).
8. Bente, F., *Ber.* **8**, 476 (1875).
9. Schultze, F., *Chem. Zentr.* **1057**, 321.
10. Fremy, E., and Terreil, A., *Compt. rend.* **66**, 456 (1868); cf. *ibid.* **48**, 862 (1859); **83**, 1136 (1876).
11. Schleiden, M. J., *Flora* **1842**, 237, quoted from Czapek, *Biochemie der Pflanzen*, Vol. 1, Jena, 1913, p. 646.
12. Muntz, A., *Compt. rend.* **94**, 453 (1882); **102**, 624, 681 (1885).
13. Schulze, E., Steiger, E., and Maxwell, W., *Z. physiol. Chem.* **14**, 227 (1890).
14. Koch, F., *Ber.* **20**, 145 (1887).
15. Thomsen, T., *J. prakt. Chem.* [2] **19**, 146 (1879).
16. Reiss, R., *Ber.* **22**, 609 (1889).
17. Schulze, E., *Ber.* **24**, 2286 (1891); Schulze, E., Steiger, E., and Maxwell, *ibid.*; Schulze, E., *Z. physiol. Chem.* **16**, 387 (1892); **19**, 38 (1894).
18. Cf. particularly Hess, K., *Die Chemie der Cellulose und ihrer Begleiter*, Leipzig, 1928, p. 7.
19. Hess, K., Wergin, W., Trogus, C., and Gundermann, J., *Papier-Fabr.* **34**, 501 (1936).
20. Hess, K., and Engel, W., *Naturwissenschaften* **28**, 143 (1940).
21. Farr, W., *Chem. Zentr.* **1939**, I, 3474.
22. Heuser, E., and Green, J. W., *Ind. Eng. Chem.* **33**, 868 (1942).
- 22 a. Hess, K., *Die Chemie der Cellulose und ihrer Begleiter*, Leipzig, 1928, p. 28.
23. Klason, P., *Tek. Tid. Uppl. C. Kemi* **23**, 56 (1893); cf. also *Svensk Papperstidn.* **20**, 176 (1917).
24. Staudinger, H., and Reinecke, E., *Holz.* **2**, 321 (1939).
25. Tollens, B., *Kurzes Handbuch der Kohlenhydrate*, 3rd ed., Leipzig, 1914, p. 561.
26. Böeseken, J., Berg, J. C., van den, and Kerstjens, A. H., *Rec. trav. chim.* **35**, 320 (1915).
27. Freudenberg, K., *Papier-Fabr.* **35**, 247 (1937).
28. Franchimont, A. P. N., *Ber.* **12**, 1941 (1879); *Compt. rend.* **92**, 1053 (1881).
29. Skraup, Z. H., and König, J., *Ber.* **34**, 1115 (1901).
30. Maquenne, L., and Goodwin, W., *Bull. soc. chim. France* [3] **31**, 854 (1904); Hardt-Stemayr, E. R. v., *Monatsh.* **28**, 63 (1907); Schiemann, W., *Ann.* **378**, 366 (1911); Ost, H., *ibid.* **393**, 335 (1913).
31. Zemplén, G., *Ber.* **59**, 1254 (1926).
32. Peterson, F. C., and Spencer, C. C., *J. Am. Chem. Soc.* **49**, 2822 (1927).
33. Ost, H., *Ann.* **393**, 335 (1913).
34. Madsen, J., *Dissertation*, Hannover, 1917.
35. Freudenberg, K., *Ber.* **54**, 767 (1921).

36. Karrer, P., and Widmer, F., *Helv. Chim. Acta* **4**, 174 (1921).
37. Kossel, W., quoted by Freudenberg, K., Tannin, Cellulose, Lignin, Berlin, 1933, p. 54.
38. Danilow, S. N., and Pastuchow, P. T., *J. Gen. Chem. (U.S.S.R.)* **17**, 1140 (1947).
39. Denham, W. S., and Woodhouse, H., *J. Chem. Soc.* **103**, 1735 (1913); **105**, 2357 (1914); **111**, 244 (1917); **119**, 81 (1921).
40. Haworth, W. N., and Leitch, C. G., *J. Chem. Soc.* **113**, 191 (1918).
41. Irvine, J. C., and Hirst, E. L., *J. Chem. Soc.* **123**, 529 (1923).
42. Haworth, W. N., *Nature* **116**, 430 (1925).
43. Charlton, W., Haworth, W. N., and Peat, S., *J. Chem. Soc.* **1926**, 89; Haworth, W. N., and Machemer, H., *J. Chem. Soc.* **1932**, 2372.
44. Bertrand, G., and Benoist, S., *Compt. rend.* **176**, 1583 (1923); **177**, 85 (1924); *Bull. soc. chim. France* [4] **33**, 1451, (1923); **35**, 58 (1924).
45. Irvine, J. C., and Robertson, G. I., *J. Chem. Soc.* **1926**, 1488.
46. Ost, H., *Z. angew. Chem.* **39**, 1117 (1926).
47. Freudenberg, K., Friedrich, K., and Bumann, I., *Ann.* **494**, 41 (1932).
48. Willstätter, R., and Zechmeister, L., *Ber.* **62**, 722 (1929).
49. Zechmeister, L., and Tóth, G., *Ber.* **64**, 857 (1931).
50. Freudenberg, K., and Friedrich, K., *Naturwissenschaften* **18**, 1114 (1930); Freudenberg, K., Andersen, C., and Go, Y., *Ber.* **63**, 1962 (1930); Freudenberg, K., and Nagai, W., *Ann.* **494**, 63 (1932).
51. Haworth, W. N., *Ber.* **56 A**, 59 (1932).
- 51a. Dickey, E. E., and Wolfrom, M. L., *J. Am. Chem. Soc.* **71**, 825 (1949).
52. Freudenberg, K., and Blomqvist, G., *Ber.* **68**, 2070 (1935); Freudenberg, K., Tannin, Cellulose, Lignin, Berlin, 1933, p. 103.
53. Cf. Meyer, K. H., and Mark, H., *Ber.* **61**, 593 (1928); *Z. physiol. Chem.* **132**, 115 (1929); Meyer, K. H., Hopf, H., and Mark, H., *Ber.* **62**, 1103 (1929); Kuhn, W., *Ber.* **63**, 1503 (1930).
54. Staudinger, H., *Papier-Fabr.* **36**, 373 (1938).
55. Pringsheim, H., *Z. physiol. Chem.* **78**, 266 (1912).
56. Karrer, P., Schubert, P., and Wehrli, W., *Helv. Chim. Acta* **3**, 797 (1925); Karrer, P., and Schubert, P., *ibid.* **9**, 893 (1926).
57. Grassmann, W., Stadler, R., and Bender, R., *Ann.* **502**, 20 (1933); Grassmann, W., Zechmeister, L., Tóth, G., and Stadler, R., *ibid.* **503**, 167 (1933).
58. Pringsheim, W., and Aronowsky, A., *Biochem. Z.* **172**, 411 (1926).
59. Weidenhagen, R., *Ergeb. Enzymforsch.* **1**, 168 (1932); Weidenhagen, R., in Bamann, E., and Myrbäck, K., *Die Methoden der Fermentenforschung*, Leipzig, 1941, p. 1903.
60. Bergmann, M., and Machemer, H., *Ber.* **63**, 316, 2304 (1930).
61. Staudinger, H., and Eder, K., *J. prakt. Chem.* [2] **159**, 39 (1941).
62. Cf. Hess, K., Dziengel, K., and Maas, H., *Ber.* **63**, 1922 (1930).
63. Schmidt, E., Meinel, K., Jandebaur, W., and Simson, W., *Cellulosechemie* **13**, 129 (1932); Schmidt, E., Schnegg, R., and Hecker, M., *Naturwissenschaften* **21**, 206 (1933).
64. Cf. Staudinger, H., *Papier-Fabr.* **36**, 373 (1938).
65. Husemann, E., and Weber, O. H., *J. prakt. Chem.* [2] **159**, 334 (1941).
66. Weber, O. H., *J. prakt. Chem.* [2] **158**, 33 (1941).
67. Heymann, E., and Rabinov, G., *J. phys. Chem.* **45**, 1152, 1167 (1941).
- 67 a. Wyk, A. J. A. van der, and Studer, M., *Helv. Chim. Acta* **32**, 1698 (1949).

68. Freudenberg, K., and Braum, E., *Ann.* **460**, 288 (1928); **461**, 130 (1928). Cf. Freudenberg, K., *Ber.* **76**, 86 (1943).
- 68a. After Hess, K., *Angew. Chem.* **49**, 841 (1936).
69. Haworth, W. N., and Machemer, H. F., *J. Chem. Soc.* **1932**, 2372; *Trans. Faraday Soc.* **29**, 14 (1933).
70. Haworth, W. N., Montonna, R. E., and Peat, S., *J. Chem. Soc.* **1939**, 1899; Haworth, W. N., Hirst, E. L., Owen, I. N., Peat, S., and Averill, F. J., *J. Chem. Soc.* **1939**, 1885.
71. Freudenberg, K., and Plankenhorn, E., *Naturwissenschaften* **26**, 124 (1938).
72. Freudenberg, K., and Boppel, H., *Ber.* **70**, 1542 (1937).
73. Freudenberg, K., Plankenhorn, E., and Boppel, H., *Ber.* **71**, 2435 (1938).
74. Freudenberg, K., and Boppel, H., *Ber.* **71**, 2505 (1938).
75. Hess, K., and Neumann, F., *Ber.* **70**, 710, 728 (1937).
76. Hess, K., Grigorescu, D., Steurer, E., and Frahm, H., *Ber.* **73**, 505 (1940).
77. Hess, K., and Steurer, E., *Ber.* **73**, 669 (1940).
78. Meyer, K. H., and Mark, H., *Der Aufbau der hochpolymeren organischen Naturstoffe*, Leipzig, 1930, p. 238.
79. Frey-Wyssling, A., *Submikroskopische Morphologie des Protoplasmas und seiner Derivate*, Berlin, 1938.
80. Karrer, P., and Escher, E., *Helv. Chim. Acta* **19**, 1192 (1936).
81. Heuser, E., *Paper Trade J.* **122**, No. 3, 43 (1946).
- 81 a. Cameron, W. G., and Morton, T. H., *Am. Dyestuff Repr.* **38**, 575 (1949).
82. Dillenius, H., *Jentgen's Kunstseide u. Zellwolle* **24**, 520 (1942).
83. Malm, C. J., and Fordyce, C. R., *Ind. Eng. Chem.* **32**, 407 (1940).
84. Yackel, E. C., and Kenyon, W. O., *J. Am. Chem. Soc.* **64**, 121 (1942).
85. Nägeli, C. v., and Schwendener, S., *Das Mikroskop*, 2nd ed., Leipzig, 1877.
86. Ambronn, H., *Ber. Verhandl. K. sächs. Ges. Wiss.* **63**, 249 (1911); *Kolloid-Z.* **21**, 185 (1917). Cf. also: J. R. Katz, *Micellartheorie und Quellung der Cellulose*, in Hess, K., *Die Chemie der Cellulose und ihrer Begleiter*, Leipzig, 1928, p. 605.
87. Zsigmondy, R., *Lehrbuch der Kolloidchemie*, 3rd ed., Leipzig, 1920, p. 408.
88. Heuser, E., *Paper Trade J.* **101**, No. 22, 35 (1935).
89. Herzog, R. O., and Jancke, W., *Ber.* **43**, 2162 (1920); *Z. Physik* **3**, 196 (1920).
90. Polanyi, M., and Weissenberg, K., *Z. Physik* **7**, 149 (1921); **9**, 123 (1922). Cf. also particularly Meyer, K. H., and Mark, H., *Der Aufbau der hochpolymeren organischen Naturstoffe*, Leipzig, 1930.
91. Polanyi, M., *Naturwissenschaften* **9**, 228 (1921); Herzog, R. O., and Gonell, H. W., *Z. physiol. Chemie* **141**, 63 (1924).
92. Karrer, P., *Cellulosechemie* **2**, 127 (1921); *Polymere Kohlenhydrate*, Leipzig, 1925.
93. Hess, K., *Z. angew. Chem.* **36**, 502 (1923); Hess, K., *Die Chemie der Cellulose und ihrer Begleiter*, Leipzig, 1928, p. 592.
94. MacGillavry, D., *Rec. trav. chim.* **48**, 18 (1929); Valko, E., *Kolloid-Z.* **51**, 130 (1930); Dohse, H., *Z. physik. Chem. A* **149**, 279, 288 (1930). See also Freudenberg, K., Bruch, E., and Rau, H., *Ann.* **460**, 228 (1928); *Ber.* **62**, 3078 (1929); **63**, 535 (1930). This idea of the small molecules also appeared later in works by Hess, K., and Ulmann, M. (*Ann.* **504**, 81 [1933]; *Ber.* **67**, 2131 [1934]; **68**, 2346 [1935]), but is nowadays abandoned.
95. Bragg, W. H., *Proc. Phys. Soc. London* **35**, 167 (1923).
96. Sponsler, O. L., and Dore, W. H., *Colloid Symposium Monograph* **4**, 174 (1926); cf. *Cellulosechemie* **11**, 185 (1930).
97. Meyer, K. H., *Ber.* **70**, 266 (1937).

98. Haworth, W. N., *J. Soc. Chem. Ind. London* **46**, 299 (1927).
99. Meyer, K. H., and Mark, H., *Ber.* **61**, 593 (1928). Cf. Meyer, K. H., *Die hochpolymeren Verbindungen*, Leipzig, 1940, p. 226.
100. Meyer, K. H., and Misch, L., *Helv. Chim. Acta* **20**, 232 (1937).
101. Mark, H., *Chem. Rev.* **26**, 169 (1940).
102. Pauling, L., *The Nature of the Chemical Bond*, Ithaca, 1944.
103. Huggins, M. L., *J. Org. Chem.* **1**, 407 (1936).
104. Ellis, J. W., and Bath, F., *J. Am. Chem. Soc.* **62**, 2859 (1940); Buswell, A. M., Downing, F. R., and Rodebush, W. H., *J. Am. Chem. Soc.* **62**, 2759 (1940).
105. Hermans, P. H., De Booys, J., and Maan, C. H., *Kolloid-Z.* **102**, 169 (1943); cf. Schiebold, E., *Beih. Z. Ver. deut. Chem. A: Chemie, B. Chem. Tech.* **1943**, No. 47, 75.
106. Freudenberg, K., and Boppel, H., *Ber.* **73**, 609 (1940).
107. Van der Wyk, A. J. A., and Meyer, K. H., *J. Polymer Sci.* **2**, 583 (1947).
108. Mark, H., and Meyer, K. H., *Z. physik. Chem.* **B2**, 115 (1929); Hess, K., Trogus, C., Akim, L., and Sakurada, A., *Ber.* **64**, 408 (1931). Kratky, O., and Sakora, A., *Naturwissenschaften* **31**, 46 (1943); *Kolloid-Z.* **108**, 169, (1944).
109. Heyn, A. N. J., *Textile Research J.* **19**, 163 (1949).
110. Berkman, S., Böhm, J., and Zoehrer, H., *Z. physik. Chem.* **124**, 83 (1926).
111. Ambronn, H., *Ber. Verhandl. K. sächs. Ges. Wiss.* **48**, 613 (1896).
112. Frey-Wyssling, A., *Protoplasma* **25**, 261 (1936); **27**, 372, 563 (1937); *Naturwissenschaften* **25**, 79 (1937); Frey-Wyssling, A., and Wälchi, O., *J. Polymer Sci.* **2**, 266 (1947).
113. Kratky, O., and Schossberger, F., *Z. physik. Chem.* **B39**, 145 (1938).
114. Brown, J. W., and Blaine, R. L., *Ind. Eng. Chem.* **39**, 1659 (1947); Emmett, P. H., *Advances in Colloid Sci.*, **1**, 1 (1942).
115. Meyer, K. H., *Kolloid-Z.* **53**, 13 (1930).
116. Meyer, K. H., *Die hochpolymeren Verbindungen*, Leipzig, 1940, p. 234.
117. Cf. Kratky, O., *Z. Papier Pappe Zellulose Holzstoff* **56**, 149 (1938); *Angew. Chem.* **53**, 153 (1940).
118. Staudinger, H., and Signer, R., *Z. angew. Chem.* **42**, 71 (1929).
119. Meyer, K. H., and Lotmar, W., *Helv. Chim. Acta* **19**, 68 (1936).
120. Schramek, W., *Papier-Fabr.* **36**, 226 (1938).
121. Gerngross, O., Hermann, K., and Abitz, W., *Z. physik. Chem.* **B10**, 371 (1930). Cf. Thiessen, R., *Angew. Chem.* **51**, 170 (1938); Hermans, P. H., *Kolloid-Z.* **98**, 76 (1938).
122. Cf. Kratky, O., *Z. physik. Chem.* **B50**, 255 (1941).
123. Sears, G. R., in Ott, E., *Cellulose and Cellulose Derivatives*, New York, 1943.
124. Wuhrmann, K., Heuberger, A., and Mühlethaler, K., *Experientia* **2**, 105, (1946); Mühlethaler, K., *Biochem. et Biophys. Acta* **3**, 15 (1949).
- 124 a. Rånby, B. G., and Ribí, E., *Experientia* **6**, 12 (1950); cf. also Svedberg, T., *Svensk Papperstidn.* **52**, 157 (1949).
- 124 b. Hock, C. W., *Textile Res. J.* **20**, 141 (1950).
125. Hermans, P. H., *J. Am. Chem. Soc.* **68**, 2730 (1946); cf. also Husemann, E., *J. makromol. Chem.* **1**, 118 (1943).
126. Hess, K., Kiessig, H., and Gundermann, J., *Z. physik. Chem.* **B 49**, 64 (1941).
127. Wergin, W., *Kolloid-Z.* **98**, 131 (1942); cf. also Frey-Wyssling, A., *Kolloid-Z.* **100**, 304 (1942); Wergin, W., *ibid.* 436.
128. Franz, E., and Schiebold, E., *J. makromol. Chem.* **1**, 3 (1943); Franz, E., Schiebold, E., and Weygand, C., *Naturwissenschaften* **31**, 350 (1943).

129. Frey-Wyssling, A., and Mühlethaler, K., *J. Polymer Sci.* **1**, 172 (1946).
130. Kratky, O., and Sekora, A., *Kolloid-Z.* **108**, 169 (1944). Cf. *Naturwissenschaften* **31**, 46 (1943).
131. Flaschner, L., and Kast, W., *Naturwissenschaften* **34**, 56 (1947).
- 131 a. Hermans, P. H., and Weidinger, A., *J. Applied Phys.* **19**, 491 (1948).
132. Hermans, P. H., Hermans, I. I., and Vermaas, D., *Kolloid-Z.* **109**, 9 (1944); Hermans, P. H., and Weidinger, *J. Am. Chem. Soc.* **68**, 1138 (1946).
133. Hermans, P. H., Hermans, I. I., and Vermaas, D., *J. Polymer Sci.* **1**, 162 (1946); cf. *J. makromol. Chem.* **1**, 247 (1944).
- 133 a. Hermans, P. H., and Weidinger, A., *J. polymer Sci.* **4**, 135 (1949).
134. Champetier, G., and Viallard, R., *Compt. rend.* **205**, 1387 (1937); Badgley, W., Frilette, V. J., and Mark, H., *Ind. Eng. Chem.* **37**, 227 (1945).
135. Mark, H., and Frilette, V. J., *Chem. Eng. News* **25**, 1260 (1947).
136. Harris, C. A., and Purves, C. B., *Paper Trade J.* **110**, No. 6, 29 (1940).
137. Assaf, A. G., Haas, R. H., and Purves, C. B., *J. Am. Chem. Soc.* **66**, 59, 66 (1944).
138. Goldfinger, G., Mark, H., and Siggia, S., *Ind. Eng. Chem.* **38**, 1083 (1943).
- 138 a. Timell, T., Dissertation, Roy. Inst. Technol., Stockholm, 1950.
- 138 b. Jorgensen, L., Dissertation, Univ., Oslo, 1950.
139. Nickerson, R. F., *Ind. Eng. Chem., Anal. Ed.* **13**, 423 (1941).
140. Nickerson, R. F., and Habrle, I. A., *Ind. Eng. Chem.* **37**, 1115 (1945); *ibid.* **38**, 299 (1946); Nickerson, R. F., and Habrle, I. A., *Ind. Eng. Chem.* **39**, 1507 (1947).
141. Philipp, H. I., Nelson, M. L., and Ziifle, H. M., *Textile Research J.* **17**, 585 (1947); Nelson, M., and Conrad, C., *Textile Research J.* **18**, 149 (1948).
142. Brenner, F. C., Frilette, V., and Mark, H., *J. Am. Chem. Soc.* **70**, 877 (1948).
143. Mark, H., *Physik und Chemie der Cellulose*, Berlin, 1932.
144. Hermans, P. H., *Contribution to the Physics of Cellulose Fibres*, Wormerveer, Holland, 1946.
- 144 a. Howsmon, J. A., *Textile Research J.* **19**, 152 (1949).
- 144 b. Hermans, P. H., and Weidinger, A., *J. polymer Sci.* **4**, 317 (1949).
145. Hess, K., Kiessig, H., and Gundermann, F., *Z. physik. Chem.* **B49**, 64 (1941).
146. Hermans, P. H., and Weidinger, A., *J. Am. Chem. Soc.* **68**, 2552 (1946).
147. Spurlin, H. M., *J. Am. Chem. Soc.* **61**, 2222 (1939).
148. Karrer, P., *Polymere Kohlenhydrate*, Leipzig, 1925, p. 232.
149. Hess, K., *Die Chemie der Cellulose*, Leipzig, 1928.
150. Lieser, Th., *Ann.* **483**, 132 (1930); **511**, 128 (1934); **522**, 56 (1936); **528**, 276 (1937); **532**, 95 (1937).
151. Schramek, W., *Papier-Fabr.* **36**, 226 (1938); Schramek, W., and Küttner, E., *Kolloid Beihefte* **42**, 331 (1935).
152. Faust, O., *Kolloid-Z.* **46**, 329 (1928).
153. Mc Bain, J. W., and Scott, D. A., *Ind. Eng. Chem.* **28**, 470 (1936).
154. Bredée, H. L., *Kolloid-Z.* **94**, 81 (1941).
155. Staudinger, H., and Daumiller, G., *Ber.* **71**, 1995 (1938); Staudinger, H., and Zapf, F., *J. prakt. Chem.* [2], **156**, 261 (1940).
156. Lieser, Th., and Fichtner, F., *Ann.* **548**, 195 (1941); Lieser, Th., and Jaks, R., *ibid.*, 204; Lieser, Th., Jaks, R., and Glitscher, E. A., *ibid.*, 212.
157. Centola, G., *Atti. Congr. intern. chim., 10th Congr., Rome* **4**, 117 (1939).
- 157 a. Desmaroux, J., and Mathieu, M., *Compt. rend.* **194**, 2053 (1932); *Trans. Faraday Soc.* **29**, 122 (1933).

- 157 b. Heuser, E., and Charbonnier, H. Y., Meeting Am. Chem. Soc. 9-13 Sept. 1940; Abstr. *Cellulosechemie* **18**, 119 (1940).
- 157 c. Stöckly, J. J., *Kolloid-Z.* **105**, 190 (1943).
- 157 d. Hermans, P. H., *Physics and Chemistry of Cellulose Fibers*, New York, 1949.
158. Cf., e.g., Hermans, P. H., and Platzek, P., *Z. physik. Chem.* **A185**, 260, 269 (1939); Hermans, P. H., *Naturwissenschaften* **28**, 223 (1940); Kargin, V. A., and Michailov, N. V., *Acta Physicochim. U.S.S.R.* **11**, 343 (1939); Hermans, P. H., *Fortschr. Chem., Physik u. Technik der makromolekularen Stoffe* **2**, 17 (1942). Cf. also Kratky, O., Sekora, A., and Treer, R., *Holz.* **4**, 273 (1941); Kratky, O., Baule, B., Sekora, A., and Treer, R., *Kolloid-Z.* **96**, 301 (1941); Brede, E., *ibid.* **94**, 81 (1941); Schramek, W., *ibid.* **94**, 92 (1941); Lieser, Th., *ibid.* **94**, 96 (1941).
- 158 a. Kratky, O., and Sekora, A., *Kolloid-Z.* **108**, 169 (1944).
- 158 b. Hermans, P. H., *Kolloid-Z.* **81**, 143 (1937); Hermans, P. H., and de Leeuw, A. J., *ibid.*, **81**, 300 (1937).
159. Lovell, E. L., and Goldschmid, O., *Ind. Eng. Chem.* **38**, 811 (1946).
160. Sisson, W. A., in E. Ott, *Cellulose and Cellulose Derivatives*, New York, 1943, p. 203.
161. Staudinger, H., Herrbach, P., and Stock, H., *Makromol. Chem.* **1**, 60 (1947).
162. Staudinger, H., *Papier-Fabr.* **36**, 373, 381 (1938).
163. Cf. comprehensive accounts with bibliographies: Staudinger, H., *Papier-Fabr.* **36**, 373, 381 (1938); Husemann, E., Plötze, E., and Schulz, G. V., *Naturwissenschaften* **29**, 257, 305 (1941); *Cellulosechemie* **18**, 121 (1940).
164. Kraemer, O., *Ind. Eng. Chem.* **30**, 1200 (1938).
165. Staudinger, H., *Die hochmolekularen organischen Verbindungen*, Berlin, 1932, p. 256.
166. Staudinger, H., Johner, H., Signer, R., Mie, G., and Hengstenberg, J., *Z. physik. Chem.* **126**, 425 (1927); Staudinger, H., *Helv. Chim. Acta* **8**, 67 (1925).
167. Einstein, A., *Ann. Physik* [4] **19**, 301 (1906).
168. Staudinger, H., *Die hochpolymeren organischen Verbindungen*, Berlin, 1932, p. 56.
169. Cf., however: Meyer, K. H., *Die hochpolymeren Verbindungen*, Leipzig, 1940, pp. 23, 568; Meyer, K. H., *Natural and Synthetic High Polymers*, New York, 1942, p. 20.
170. Dörr, R. E., *Angew. Chem.* **53**, 50 (1940).
171. Schieber, W., *Papier-Fabr.* **37**, 245 (1939).
172. Löbering, J., *Die Chemie* **55**, 91 (1942).
173. Kleine, J., *Die Chemie* **55**, 179 (1942).
174. Zart, A., *Kleipzig's Textil-Z.* **9**, 272 (1941).
175. Staudinger, H., *Papier-Fabr.* **36**, 473 (1938).
- 175 a. Sookne, A. M., and Harris, M., *Ind. Eng. Chem.* **37**, 478 (1945).
176. Eisenhut, O., and Kuhn, E., *Die Chemie* **55**, 198 (1942).
- 176 a. Welch, L. M., Roseveare, W. E., and Mark, H., *Ind. Eng. Chem.* **38**, 580 (1946).
177. Cf. Kern, W., *Ber.* **68**, 1439 (1938); Schulz, G. V., *Z. physik. Chem.* **B30**, 379 (1935); **B32**, 27 (1936); **B40**, 102 (1938); Kraemer, E. O., and Lansing, W. D., *J. Am. Chem. Soc.* **57**, 1369 (1935); **58**, 1471 (1936); Kraemer, O., *Ind. Eng. Chem.* **30**, 1200 (1938). More literature in Meyer, K. H., *Natural and Synthetic High Polymers*, New York, 1942, p. 20; and Meyer, K. H., *Die hochpolymeren Verbindungen*, Leipzig, 1940, p. 24.

178. Cf. Svedberg, T., *Kolloid-Z.* **67**, 2 (1934); Lamm, O., *Kolloid-Z.* **69**, 44 (1934); Signer, R., and Gross, H., *Helv. Chim. Acta* **17**, 726 (1934); Svedberg, T., *Cellulosechemie* **21**, 57 (1943); and especially: Mitchell, R. L., *Ind. Eng. Chem.* **38**, 843 (1946); Tasman, J. E., and Covey, A. J., *Pulp Paper Mag. Can.* **48**, No. 3, 166 (1947).
179. Staudinger, H., and Heuer, W., *Z. physik. Chem.* **A171**, 129 (1934).
180. Stamm, A. J., in Wise, L. E., *Wood Chemistry*, New York, 1946, p. 165.
181. Jullander, I., and Svedberg, T., *Nature* **153**, 523 (1944).
182. Jullander, I., *Arkiv Kemi. Mineral. Geol.* **21A**, No. 8 (1945).
183. Svedberg, T., *J. Phys. & Colloid Chem.* **51**, 1 (1947).
- 183 a. Enoksson, B., *J. polymer Sci.*, **3**, 314 (1948).
184. Svedberg, T., and Pedersen, K. O., *The Ultracentrifuge*. Oxford Univ. Press, London, 1940.
185. Stamm, A. J., *J. Am. Chem. Soc.* **52**, 3047, 3062 (1930).
186. Kraemer, E. O., and Lansing, W. D., *Nature* **133**, 870 (1934); *J. Phys. Chem.* **39**, 153 (1935); Kraemer, E. O., *Ind. Eng. Chem.* **30**, 1200 (1938); Kraemer, E. O., and Nichols, J. B., in Svedberg, T., and Pedersen, K. O., *The Ultracentrifuge*, London, 1940, p. 418.
187. Jullander, I., *J. Polymer Sci.* **2**, 329 (1947).
188. Gralén, N., and Svedberg, T., *Nature* **152**, 625 (1943).
189. Gralén, N., Dissertation, Univ., Uppsala, 1944.
190. Gralén, N., and Rånby, B., in *The Svedberg, 1884—1944*, Uppsala, 1944, p. 274; Gralén, N., and Samuelson, O., *Svensk Papperstidn.* **48**, 1 (1945); Gralén, N., *Kolloid-Z.* **95**, 188 (1941).
191. Mosimann, H., *Helv. Chim. Acta*, **26**, 61, 369 (1943); Mosimann, H., and Signer, R., *ibid.* **27**, 1123 (1944).
192. Bryde, O., and Rånby, B., *Svensk Papperstidn.* **50**, No. 11B, (Jubilee Vol. E. Hägg-lund), 34 (1947).
193. Debye, P., *J. Applied Phys.* **15**, 338 (1944); *J. Phys. & Colloid Chem.* **51**, 18 (1947).
194. Stein, R. S., and Doty, P. M., *J. Am. Chem. Soc.* **68**, 159 (1946).
195. Mark, H., *Frontiers in Chem.*, **5**, 121 (1948).
196. Kratky, O., and Mark, H., *Papier-Fabr.* **36**, 345 (1938).
197. Kuhn, W., *Kolloid-Z.* **68**, 2 (1934); *Z. physik. Chem.* **A175**, 1 (1936). Cf. Freudenberg, K., *Papier-Fabr.* **34**, 503 (1936).
198. Müller, F. H., *Beih. Z. Ver. deut. Chem. A: Chemie, B: Chem. Tech.* **1943**, No. 47, 81.
199. Kratky, O., *Angew. Chem.* **53**, 157 (1940). Cf. Hermans, P., *Kolloid-Z.* **96**, 311 (1942).
200. Schramek, W., Metzner, U., and Seidel, E., *Z. physik. Chem.* **B50**, 298 (1941).
201. Mosimann, H., *Helv. Chim. Acta* **26**, 61 (1943).
202. Neubauer, Th., *Ann. Physik [5]* **42**, 503 (1943).
203. Hermans, I. I., *J. Polymer Sci.* **1**, 233 (1946).
204. Katz, J. R., *Ergeb. exakt. Naturw.* **3**, 316 (1924); **4**, 154 (1925).
205. Cf. Hess, K., and Trogus, C., *Ergeb. techn. Röntgenk.* **4**, 41 (1934).
206. Cf. Meyer, K. H., *Die hochpolymeren Verbindungen*, Leipzig, 1940, p. 132.
207. Cf. Hess, K., *Naturwissenschaften* **22**, 473 (1934).
208. Cf. K. H. Meyer, *Die hochpolymeren Verbindungen*, Leipzig, 1940, p. 231, 268. *Natural and Synthetic High Polymers*, New York, 1942, p. 284.
209. Meyer, K. H., and Badenhuisen, N. P., *Nature* **140**, 281 (1937).

210. Girard, A., *Ann. chim. et phys.* [5] **24**, 350 (1881); *Compt. rend.* **38**, 1323 (1877); Tollens, B., Muruchow, J. J., and Sack, J., *Ber.* **34**, 1431 (1901); Knoevenagel, E., and Busch, H., *Cellulosechemie* **3**, 42 (1922); Heuser, E., Neuenstein, W. v., Eisenring, F., and Schott, W., *Cellulosechemie* **3**, 89 (1922); **4**, 13, 85 (1923); Birtwell, C., Clibbens, D. A., and Geake, A., *J. Textile Inst.* **17**, T145 (1926).
211. Netthöfel, W., Dissertation, Berlin, 1914; Hauser, O., and Herzfeld, H., *Chem.-Ztg.* **39**, 689 (1915); Heuser, E., *The Chemistry of Cellulose*, New York, 1914, p. 9, 493.
212. Herzog, R. O., *Papier-Fabr.* **23**, 121 (1926).
213. Knoevenagel, E., and Busch, H., *Cellulosechemie* **3**, 42 (1922).
214. Hess, K., *Die Chemie der Cellulose und ihrer Begleiter*, Leipzig, 1928, p. 450.
215. Hess, K., *Die Chemie der Cellulose und ihrer Begleiter*, Leipzig, 1928, pp. 448, 270. Cf. Katz, J. R., Micellartheorie und Quellung der Cellulose, *ibid.*, p. 605.
216. Lieser, Th., *Angew. Chem.* **49**, 759 (1936).
217. Hiller, L. A., Jr., and Pacsu, E., *Textile Research J.* **16**, 490 (1946); Pacsu, E., *Textile Research J.* **17**, 405 (1947).
218. Lüdtkke, M., *Ann.* **456**, 201 (1927); 466, 38 (1928); *Biochem. Z.* **233**, 1 (1933).
219. Hess, K., Trogus, C., Akim, L., and Sakurada, J., *Ber.* **64**, 408 (1931); Hess, K., and Akim, L., *Cellulosechemie* **12**, 95 (1931); Hess, K., and Rabinowitsch, B., *Kolloid-Z.* **64**, 257 (1933); Hess, K., and Trogus, C., *Kolloid-Z.* **68**, 169 (1934); Hess, K., *Melliand Textilber.* **15**, 29, 65 (1934).
220. Staudinger, H., and Sorkin, M., *Ber.* **70**, 1565 (1937).
221. Cf. Freudenberg, K., and Blomqvist, G., *Ber.* **68**, 2070 (1935); Ekenstam, A. af, *Ber.* **69**, 553 (1936); Dissertation, Lund, 1936.
222. Battista, O. A., and Coppick, S., *Textile Research J.* **17**, 419 (1947).
223. Pacsu, E., *Textile Research J.* **17**, 405 (1947).
224. Haworth, W. N., Peat, S., and Wilson, W. J., *J. Chem. Soc.* **1939**, 1904.
225. Martin, A. R., Smith, L., Whistler, R. L., and Harris, M., *J. Research Natl. Bur. Standards* **27**, 449 (1941).
226. Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.* **19**, T389 (1928).
227. Bujewskoi, A., *Chem. Zentr.* **1941**, I, 3224.
228. Comprehensive literature until 1928 in Hess, K., *Die Chemie der Cellulose und ihrer Begleiter*, Leipzig, 1928, p. 455.
229. Staudinger, H., and Reinecke, F., *Melliand Textilber.* **20**, 109, (1939).
230. Eisenhut, O., *J. prakt. Chem.* [2] **157**, 338 (1941).
231. Cf. Weltzien, W., Tobel, G. zum, *Ber.* **60**, 2024 (1927); Götze, K., *Kunstseide und Zellwolle nach dem Viscoseverfahren*, Berlin, 1940, p. 232; Zart, A., *Ergeb. angew. physik. Chem.* **2**, 254 (1935).
232. Staudinger, H., and Jurisch, J., *Papier-Fabr.* **35**, 459 (1939).
233. Kalb, L., and Falkenhausen, F. v., *Ber.* **60**, 2514 (1927).
234. Kenyon, W. O., and Yackel, E. C., *J. Am. Chem. Soc.* **64**, 121 (1942); Unruh, C. C., and Kenyon, W. O., *ibid.* **64**, 127 (1942); Taylor, E. W., Fowler, W. F., Jr., McGee, P. A., and Kenyon, W. O., *ibid.* **69**, 342 (1947); McGee, P. A., Fowler, W. F., Jr., and Kenyon, W. O., *ibid.* **69**, 347 (1947); Unruh, C. C., McGee, P. A., Fowler, W. F., Jr., Kenyon, W. O., *ibid.* **69**, 349 (1947); McGee, P. A., Fowler, W. F., Jr., Taylor, E. W., Unruh, C. C., and Kenyon, W. O., *ibid.* **69**, 355 (1947).
235. Maurer, K., and Reiff, G., *J. makromol. Chem.* **1**, 27 (1943).
- 235 a. Pigman, W. M., Browning, B. L., McPherson, W. H., Calkins, C. R., and Leaf Jr., R. L., *J. Am. Chem. Soc.* **71**, 2200 (1949).

- 235 b. Kenyon, R. L., Hasek, R. H., Davy, L. G., and Broadbooks, K. J., *Ind. Eng. Chem.* **41**, 2 (1949).
236. Davidson, G. F., *J. Textile Inst.* **25**, T174 (1934), 27, T144 (1936).
237. Staudinger, H., and Roos, E., *Melliand Textilber.* **22**, 369 (1941).
238. Jackson, E. L., and Hudson, C. S., *J. Am. Chem. Soc.* **58**, 378 (1936), **59**, 994, 2049 (1937), **60**, 989 (1938).
239. Davidson, G. F., *J. Textile Inst.* **31**, T81 (1940), **32**, T109 (1941).
240. Rutherford, H. A., Minor, F. W., Martin, A. R., and Harris, M., *J. Research Natl. Bur. Standards* **29**, 131 (1942); *Am. Dyestuff Repr.* **31**, 399 (1942).
241. Heidt, L. J., Gladding E. K., and Purves, C. B., *Paper Trade J.* **121**, No. 9, 35 (1945).
242. Jayme, G., Sâtre, M., and Maries, S., *Naturwissenschaften* **29**, 768 (1941).
243. Staudinger, H., and Eder, K. W., *Cellulosechemie* **19**, 125 (1941).
244. Pacsu, E., *Textile Research J.* **15**, 354 (1945).
245. Gehman, H., Kreider, L. C., and Evans, W. L., *J. Am. Chem. Soc.* **58**, 2388 (1936).
246. Head, F. S. H., *Shirley Institute Memoirs (England)* **21**, 11 (1947).
247. Bergek, T., Gustavsson, S., and Lindvall, E., *Svensk Papperstidn.* **50**, No. 11B (Jubilee. Vol. E. Hägglund), 22 (1947).
248. Goldfinger, G., Mark, H., and Siggia, S., *Ind. Eng. Chem.* **35**, 1083 (1943).
249. Müller, F., *Helv. Chim. Acta* **22**, 208, 217 (1939); **29**, 130 (1946).
250. Gladding, E. K., and Purves, C. B., *Paper Trade J.* **116**, No. 14, 26 (1943); Meesook, B., and Purves, C. B., *Paper Trade J.* **123**, No. 18, 35 (1946).
251. Geiger, E., *Schweiz. Chem.-Ztg.* **27**, 95 (1944); *Helv. Chim. Acta* **28**, 1159 (1945).
252. Wilson, K., *Svensk Papperstidn.* **51**, 45 (1948).
253. Marschall, A., *Jentgen's Kunstseide u. Zellwolle* **24**, 462 (1942). Cf. Tydén, H., Dissertation, Stockholm, 1942.
254. Hess, K., Kiessig, H., and Gundermann, J., *Z. physik. Chem.* **B49**, 64 (1941).
255. Carolles, B. de, *J. prakt. Chem.* [1] **32**, 427 (1844).
256. Fehling, H., *Ann.* **53**, 134 (1845).
257. Marchand, R. F., quoted by Kalinowsky, W., *J. prakt. Chem.* [1] **35**, 199 (1845).
258. Hönig, M., and Schubert, S., *Monatsh.* **6**, 708 (1885); **7**, 455 (1886).
259. Stern, A. L., *J. Chem. Soc.* **67**, 74 (1895).
260. Champetier, G., and Bonnet, J., *Bull. soc. chim. France* [5] **10**, 585 (1943).
261. Ekenstam, A. af, Dissertation, Lund, 1936, p. 73.
262. Cf. Ekenstam, A. af, Dissertation, Lund, 1936, p. 49.
263. Cf. Stamm, A. J., and Cohen, W. E., *J. Phys. Chem.* **42**, 921 (1938).
264. Freudenberg, K., Kuhn, W., Dürr, W., Bolz, F., and Steinbrunn, G., *Ber.* **63**, 1510 (1930); Freudenberg, K., and Kuhn, W., *Ber.* **65**, 484 (1932); Freudenberg, K., and and Blomqvist, G., *Ber.* **68**, 2070 (1935).
265. Staudinger, H., *Cellulosechemie* **15**, 66 (1934).
266. Freudenberg, K., and Blomqvist, G., *Ber.* **68**, 2079 (1935).
267. Schulz, G. V., and Lohmann, H. J., *J. prakt. Chem.* [2] **157**, 238 (1941).
- 267 a. Sillén, L. G., *Svensk Kem. Tid.* **55**, 221, 266 (1943).
- 267 b. Kuhn, W., *Z. physik. Chem.* **A159**, 368 (1932).
268. Schulz, G. V., and Husemann, E., *Z. physik. Chem.* **B52**, 23 (1942).
269. Husemann, E., and Weber, O. H., *J. prakt. Chem.* [2] **159**, 334 (1942).
- 269 a. Schulz, G. V., and Husemann, E., *Z. Naturforsch.* **1**, 268 (1946); Schulz, G. V., *J. Polymer Sci.* **3**, 365 (1948).
270. Sihtola, H., Dissertation, Helsingfors, 1944.

- 270 a. Husemann, E., and Carnap, A., *J. makromol. Chem.* **1**, 16 (1943); *ibid.* **1**, 158 (1943); Husemann, E., *Naturwissenschaften* **32**, 79 (1944).
271. Paesu, E., *Progress in the Chemistry of Organic Natural Products* **5**, 128 (1948). Cf., however, Husemann, E., and Consbruch, U., *Makromol. Chem.* **5**, 179 (1950).
272. Banderet, A., and Rånby, B., *Helv. Chim. Acta* **30**, 1190 (1947).
273. Bergek, T., *Norsk Skogindustri* **2**, 289 (1948).
274. Rånby, B. G., *Acta Chem. Scand.* **3**, 649 (1949).
- 274 a. Rånby, B. G., *Norsk Skogindustri* **1**, 295 (1947).
- 274 b. Kinell, P. O., and Rånby, B. G., *Advances in Colloid Science* **3**, 161 (1949).
- 274 c. Hengstenberg, J., and Mark, H., *Z. Krist.* **69**, 271 (1928).
275. Simonsen, E., *Z. angew. Chem.* **11**, 195 (1898).
276. Reiferscheidt, E., *Z. angew. Chem.* **18**, 47 (1905); Koerner, T., *Z. angew. Chem.* **21**, 2353 (1908).
277. Neuman, J., Dissertation, Dresden, 1910, p. 31; Ost, H., and Wilkening, L., *Chem.-Ztg.* **34**, 461 (1910).
278. Ost, H., and Brodtkorb, Th., *Chem.-Ztg.* **35**, 1125 (1911).
279. Wohl, A., and Blumrich, K., *Z. angew. Chem.* **34**, 17 (1921). Cf. Wohl, A., *Ber.* **23**, 2097 (1890).
280. Hägglund, E., *Medd. Cellulosaind. Centrallaboratorium (Stockholm)*, Ser. B, No. 5 (1941).
281. Lüers, H., *Z. angew. Chem.* **43**, 455 (1930); *Angew. Chem.* **45**, 369 (1932).
282. Scholler, H., Dissertation, München, 1923.
283. Saeman, J. F., *Ind. Eng. Chem.* **37**, 43 (1945).
284. Kuhn, W., *Ber.* **63**, 1503 (1930); Freudenberg, K., *Ber.* **65**, 484 (1932). Cf. Klages, F., *Ber.* **65**, 302 (1932); Ekenstam, A. af, *Ber.* **69**, 553 (1936); Dissertation, Lund, 1936.
285. Freudenberg, K., and Soff, K., *Ber.* **66**, 19 (1933).
286. Ant-Wuorinen, O., *Papir-J.* **27**, 307, 322 (1939).
287. Schwalbe, C. G., *Chemie der Cellulose*, 2nd ed., Berlin, 1938, p. 172.
288. Bujewskoi, A., *Chem. Zentr.* **1941**, I, 3224; Bujewskoi, A., and Wedenjew, W., *Chem. Zentr.* **1941**, I, 3224.
289. Nickerson, R. F., *Ind. Eng. Chem.* **33**, 1022 (1941).
290. Nickerson, R. F., *Ind. Eng. Chem., Anal. Ed.* **13**, 423 (1941).
291. Reeves, R. E., Schwartz, W. M., and Giddens, J. E., *J. Am. Chem. Soc.* **68**, 1383 (1946).
292. Willstätter, R., and Zechmeister, L., *Ber.* **46**, 2995 (1913); Zechmeister, L., *Z. physiol. Chem.* **103**, 216 (1923).
293. Heuser, E., and Boedeker, E., *Z. angew. Chem.* **34**, 462 (1921).
294. Ost, H., *Ber.* **46**, 2995 (1913).
295. Frahm, H., *Ber.* **74**, 622 (1941).
296. Cf. Coleman, G. H., Buchanan, M. A., and Paul, Ph. T., *J. Am. Chem. Soc.* **57**, 1119 (1935); Hurd, Ch. B., and Cantor, G. M., *J. Am. Chem. Soc.* **60**, 2677 (1938).
297. Sherrard, E. C., and Froehle, A. W., *J. Am. Chem. Soc.* **45**, 1720 (1923).
298. Hess, K., and Friese, H., *Ann.* **456**, 42 (1927).
299. Wolf from, M. L., and Georges, L. W., *J. Am. Chem. Soc.* **59**, 282 (1937).
300. Hibbert, H., and Percival, E. G. V., *J. Am. Chem. Soc.* **52**, 3995 (1930).
301. Wolf from, M. L., Sowden, J. C., and Lassetre, E. N., *J. Am. Chem. Soc.* **61**, 1072 (1939).

302. Kiesel, A., and Semiganowski, N., *Ber.* **60**, 333 (1927). Cf. Lüdtkke, M., *Ann.* **456**, 222 (1927).
303. Häggglund, E., and Bratt, L. C., *Svensk Kem. Tid.* **48**, 125 (1936).
304. Saeman, J. F., Bubl, Z. L., and Harris, E. E., *Ind. Eng. Chem., Anal. Ed.* **17**, 35 (1945).
305. Schlubach, H. H., Elsner, H., and Prochownick, V., *Angew. Chem.* **45**, 245 (1932).
306. Hess, K., and Ulmann, M., *Ber.* **74**, 119 (1941).
307. Schlubach, H. H., and Prochownick, V., *Angew. Chem.* **47**, 132 (1934).
308. Schlubach, H. H., and Lührs, E., *Ann.* **547**, 73 (1941).
309. Hess, K., Stricker, F., and Rutkowski, R., *Cellulosechemie* **21**, 125 (1943).
310. Helferich, B., and Böttger, St., *Ann.* **476**, 150 (1929).
311. Fredenhagen, K., and Cadenbach, G., *Z. anorg. u. allgem. Chem.* **178**, 289 (1929).
312. Pictet, A., and Sarasin, J., *Helv. Chim. Acta* **1**, 87 (1918).
313. Venn, H. J. P., *Cellulosechemie* **5**, 95 (1924).
314. Tauss, H., *Dinglers Polytech. J.* **276**, 411 (1890).
315. Hoppe-Seyler, F., *Z. physiol. Chem.* **13**, 66 (1889).
316. Fischer, F., and Schrader, H., *Ges. Abhandl. Kenntnis Kohle* **5**, 339 (1922).
317. Schwalbe, C. G., and Becker, E., *Zellstoff u. Papier* **1**, 100 (1921).
318. Tollens, B., Sack, I., and Muruchow, J. J., *Ber.* **34**, 1427 (1901).
319. Heuser, E., and Herrmann, F., *Cellulosechemie* **5**, 1 (1924).
320. Bergius, F., and Specht, H., Die Anwendung hoher Drucke bei chemischen Vorgängen etc., Halle, 1913, p. 47.
321. Tropsch, H., and Philippovich, A. v., *Ges. Abhandl. Kenntnis Kohle* **7**, 84 (1925).
322. Bergius, F., and Erasmus, P., *Naturwissenschaften* **16**, 1 (1928); *Svensk Kem. Tid.* **39**, 189 (1927).
- 322 a. Anon., *Chem. Eng. News* **25**, 2452 (1947).
- 322 b. Asplund, A. J. A., U. S. Pat. 2,008,892 (1935).
Löwgren, U., *Paper Trade J.* **113**, No. 11, 29 (1941).
323. Aronovsky, S. I., and Gortner, R. A., *Ind. Eng. Chem.* **35**, 305 (1933).
324. Schwalbe, C. G., *Chemie der Cellulose*, 2nd ed., Berlin, 1938, p. 62.
325. Dore, W. H., *Ind. Eng. Chem.* **12**, 475 (1920).
326. Overbeck, W., and Müller, H. F., *Ber.* **75**, 547 (1942).
327. Schütz, F., *Ber.* **75**, 703 (1942).
328. Schütz, F., and Sarten, P., *Cellulosechemie* **21**, 35 (1943).
329. Pictet, A., and Sarasin, J., *Helv. Chim. Acta* **1**, 87 (1918); cf. *ibid.* 81.
330. Chorley, J. C., and Ramsay, W., *J. Soc. Chem. Ind. London* **11**, 872 (1892).
331. Klason, P., Heidenstam, G. v., and Norlin, E., *Arkiv Kemi, Mineral. Geol.* **3**, No. 1 (1907).
332. Wislicenus, H., and Büttner, G., *J. prakt. Chem.* [2] **79**, 177 (1909).
333. Erdmann, E., and Schaefer, C., *Ber.* **43**, 2398 (1910).
334. Fischer, F., and Schneider, W., *Ges. Abhandl. Kenntnis Kohle* **3**, 290 (1918).
335. Fischer, F., and Schrader, H., *Ges. Abhandl. Kenntnis Kohle* **5**, 113 (1922).
336. Fischer, F., and Niggemann, H., *Ges. Abhandl. Kenntnis Kohle* **1**, 176 (1915).
337. Quoted from Omelianski, W., Die Cellulosegärung, in F. Lafar, *Handbuch der technischen Mykologie*, vol. 3, Jena, 1904-06.
338. Enebo, L., *Acta Agr. Suecana* **2**, 319, (1947).
339. Clausen, P., *Zentr. Bakt. Parasitenk. Abt. II*, **84**, 20 (1931).
340. Macfadyen, A., and Blaxall, F. R., *Trans. Jenner Inst. Prev. Med., Seed. ser.* 162 (1899).

341. Enebo, L., *Svensk Kem. Tid.* **60**, 176 (1948); *Nature* **163**, 805 (1949).
- 341 a. Mc Bee, R. M., *J. Bact.* **56**, 653 (1948).
342. Norman, A. G., *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.*, Oxford, 1937, p. 30.
343. Stanier, R. Y., *J. Bact.* **40**, 619 (1940).
344. van Iterson, G., *Zentr. Bakt. Parasitenk. Abt. II*, **11**, 689 (1904).
345. Hutchinson, H. B., and Clayton, J., *J. Agr. Sci.* **9**, 143 (1919).
346. Winogradsky, S., *Ann. Inst. Pasteur* **43**, 549 (1929).
347. Krzemieniewska, H., *Acta Soc. Botan. Poloniae* **7**, 507, (1930).
348. Fåhræus, G., *Ann. Agr. Coll. Sweden* **12**, 1 (1944); *Symbolae Botan. Upsaliensis* **9** (2) (1947).
349. Langwell, H., *J. Soc. Chem. Ind. London* **51**, 988 (1932); British Pat. 134, 265 (1919), 161,294 (1921), 248,795 (1926), 271,254 (1927), 334,900 (1930); Canadian Pat. 222,960 (1922), 234,367 (1923), 282,038 (1928), 282,039 (1928); U. S. Pat. 1,443,881 (1923), 1,602,306 (1926), 1,639,571 (1927).
350. Enebo, L., *Svensk Papperstidn.* **51**, 157 (1948).
351. Pringsheim, H., *Z. physiol. Chem.* **78**, 266 (1912).
352. Norman, A. G., *Cellulose Decomposition by Microorganisms*, in *Malisoff*, *Dictionary of Biochemistry*, New York 1943, p. 125.
353. Virtanen, A. L., *Adaption and Uptake of Nutrition by Microorganisms in Intern. Congr. Microbiology Rept. Proc. 4th Congr.*, Copenhagen 1947, p. 121.
354. Virtanen, A. L., and Nikkilä, O. E., *Suomen Kemistilehti* **19B**, 3 (1946). — Virtanen, A. I., and Hukki, J., *Suomen Kemistilehti* **19B**, 4 (1946). — Virtanen, A. I., Koistinen, O., and Kiuru, V., *Suomen Kemistilehti* **11B**, 30 (1938).
355. Olson, F. R., Peterson, W. H., and Sherrard, E. C., *Ind. Eng. Chem.* **29**, 1026 (1937).
356. Veldhuis, M. K., Christensen, L. M., and Fulmer, E. I., *Ind. Eng. Chem.* **28**, 430 (1936).
357. Virtanen, A. I., *Nature* **158**, 795 (1946).
358. Neuberg, C., and Cohn, R., *Biochem. Z.* **139**, 527 (1923).
359. Nord, F. F., and Vitucci, J. C., *Nature* **160**, 224, 260 (1947); *Arch. Biochem.* **14**, 243 (1947).
360. Meyer, K. H., *Natural and Synthetic High Polymers*, New York, 1942, p. 328.
361. Mark, H., *Melliand Textilber.* **10**, 695 (1929); Boer, J. H. de, *Trans. Faraday Soc.* **32**, 10 (1935); Hermans, P. H., *Rec. trav. chim.* **58**, 63 (1939).
362. Schmidhäuser, O., *Melliand Textilber.* **17**, 905 (1936).
363. Staudinger, H., and Sorkin, M., *Ber.* **70**, 1570 (1937).
364. Franz, E., and Henning, H. J., *Melliand Textilber.* **17**, 121 (1936).
365. Staudinger, H., and Dreher, E., *Ber.* **69**, 1091 (1936).
366. Steurer, E., *Chem. Tech. Berlin* **16**, 1 (1943). Cf. Hess, K., and Heumann, K. E., *Ber.* **75**, 1802 (1942).
367. Hess, K., Kiessig, H., and Gundermann, J., *Z. physik. Chem.* **B49**, 64 (1941). Cf. Hermans, P. H., and Weidinger, A., *J. Am. Chem. Soc.* **68**, 343, 2547, 2730 (1946).
368. Heuser, E., and Haug, A., *Z. angew. Chem.* **34**, 461 (1921).
369. Heuser, E., and Boedeker, E., *Z. angew. Chem.* **34**, 461 (1921).
370. Wise, L. E., and Russell, W. C., *Ind. Eng. Chem.* **14**, 285 (1922).
371. Wise, L. E., and Russell, W. C., *Ind. Eng. Chem.* **15**, 815 (1923).
372. Heuser, E., and Dammel, W., *Cellulosechemie* **5**, 52 (1924).
373. Irvine, J. C., and Hirst, E. L., *J. Chem. Soc.* **121**, 1585 (1922); **125**, 15 (1924).
374. Sherrard, E. C., and Blanco, G. W., *J. Am. Chem. Soc.* **45**, 1010 (1923).

375. Sherrard, E. C., and Aiyar, S. S., *Cellulosechemie* **5**, 46 (1924).
376. Heuser, E., and Aiyar, S. S., *Z. angew. Chem.* **37**, 27 (1924).
377. Ost, H., and Wilkening, L., *Chem.-Ztg.* **35**, 1125 (1911).
378. Monier-Williams, G. W., *J. Chem. Soc.* **119**, 803 (1921).
379. Lenze, F., Pleus, B., and Müller, J., *J. prakt. Chem.* [2] **101**, 213 (1921).
380. Fromherz, K., Dissertation, Strassburg, 1906.
381. Schulze, E., and Godet, Ch., *Z. physiol. Chem.* **61**, 233 (1909).
382. Häggglund, E., and Klingstedt, F. W., *Cellulosechemie* **5**, 57 (1924); Klingstedt, F. W., *Z. anal. Chem.* **66**, 129 (1925). Cf. Gierisch, W., *Cellulosechemie* **6**, 61, 81 (1925).
383. Schwalbe, C. G., and Schrimpff, A., *Z. angew. Chem.* **27**, 662 (1914); *Z. ges. Schiess- u. Sprengstoffw.* **14**, 41 (1919); Schrimpff, A., *Z. ges. Schiess- u. Sprengstoffw.* **14**, 185 (1919); Lenze, F., Pleus, B., and Müller, J., *J. prakt. Chem.* [3] **101**, 213 (1921); Wells, S. D., and Edwards, V. P., *Paper* **25**, No. 23, 180, (1919).
384. Nauck, W., *Cellulosechemie* **2**, 61 (1921).
385. Häggglund, E., Löfman, N., and Färber, E., *Cellulosechemie* **3**, 13 (1922).
386. Debye, P., and Scherrer, P., *Physik. Z.* **17**, 277 (1916); **18**, 291 (1917).
387. Wise, L. E., *Ind. Eng. Chem.* **15**, 713 (1923).
388. Klason, P., *Svensk Papperstidn.* **27**, 261 (1924).
389. Cf. Häggglund, E., *Holzchemie*, 1st ed., Leipzig, 1928, p. 56.
390. Bell, D. J., *Biochem. J.* **26**, 590, 598, 609 (1932).
391. Karrer, P., and Escher, E., *Helv. Chim. Acta* **19**, 1192 (1936).
392. Barsha, J., and Hibbert, H., *J. Am. Chem. Soc.* **58**, 1006 (1936).
393. Staudinger, H., Dreher, E., *Zellstoff-Faser* **33**, 163 (1936); Staudinger, H., Dreher, E., and Jurisch, I., *Ber.* **70**, 2502 (1937).
394. Schmidt, E., and Graumann, E., *Ber.* **54**, 1863 (1921).
395. Staudinger, H., and Husemann, E., *Holz Roh- u. Werkstoff* **4**, 343 (1941).
396. Klauditz, W., *Papier-Fabr.* **39**, 225 (1941).
397. Dolmetsch, H., and Reinecke, Fr., *Chem. Zentr.* **1940**, I, 154.
398. Blaker, R. H., Badger, R. M., and Noyes, R. M., *J. Phys. & Colloid Chem.* **51**, 574 (1947).
399. Mitchell, R. L., *Ind. Eng. Chem.* **38**, 843 (1946). Cf. also Atchinson, R. L., *Paper Trade J.* **116**, No. 22, 23 (1943); Schieber, W., *Papier-Fabr.* **37**, 245 (1939).
400. Coppick, S., *Paper Trade J.* **117**, No. 26, 29 (1943).
401. Gralén, N., Dissertation, Uppsala, 1944, p. 65. Cf. Golova, O. P., *Chem. Abstr.* **40**, 457 (1946); Golova, O. P., and Ivanov, V. I., *Bull. acad. sci. U.R.S.S.* 1945, 279; *Chem. Abstr.* **40**, 1653 (1946).
402. Renker, M., *Über Bestimmungsmethoden der Cellulose*, Berlin, 1910. Cf. the collation by Häggglund, E., in Schwalbe, C. G., *Die chemische Untersuchung pflanzlicher Rohstoffe etc.*, Berlin, 1920, p. 110.
403. Cf. particularly Freudenberg, K., Belz, W., and Niemann, Chr., *Ber.* **62**, 1554 (1929).
404. Cross, C. F., and Bevan, E. J., *J. Chem. Soc.* **55**, 199 (1889); Cross, C. F., and Bevan, E. J., *Cellulose*, N. Y., 1918, p. 95.
405. Dean, A. L., and Tower, G. E., *J. Am. Chem. Soc.* **29**, 1119 (1907).
406. Renker, M., *Über Bestimmungsmethoden der Cellulose*, Berlin, 1910, p. 46.
407. Cf. also Ritter, G. F., and Fleck, L. C., *Ind. Eng. Chem.* **16**, 147 (1924).
408. Renker, M., *Über Bestimmungsmethoden der Cellulose*, Berlin, 1910, p. 47.
409. Fremy, E., and Terreil, A., *Bull. soc. chim. France* [2] **9**, 439 (1868).

410. Cf. Sieber, R., *Zellstoff u. Papier* **3**, 27 (1923).
411. Ritter, G. J., and Mitchell, R. L., *U. S. Forest Products Lab. Mimeograph* R 1028, Apr. 1934; *Chem. Abstr.* **29**, 6047 (1935).
412. Müller, H., *Die Pflanzenfaser*, Braunschweig, 1917, p. 27.
413. Renker, M., *Über Bestimmungsmethoden der Cellulose*, Berlin, 1910, p. 68.
414. Cross, C. F., and Bevan, E. J., *Cellulose*, N. Y., 1918, pp. 116, 148.
415. Zeisel, S., and Stritar, M. J., *Ber.* **36**, 1252 (1902).
416. Mulder, G. J., *J. prakt. Chem.* [1] **39**, 152 (1846).
417. Cross, C. F., and Bevan, E. J., *Cellulose*, N. Y., 1918, p. 97.
418. Schulze, F., *Chem. Zentr.* **1857**, 321.
419. Henneberg, W., *Ann.* **146**, 130 (1868).
420. Cross, C. F., and Bevan, E. J., *Cellulose*, N. Y., 1918, p. 146.
421. Schwalbe, C. G., German Pat. 204,460 (1907).
422. Hoffmeister, W., *Chem. Zentr.* **1887**, 1412.
423. Renker, M., *Über Bestimmungsmethoden der Cellulose*, Berlin, 1910, p. 77.
424. Lifschütz, J., *Ber.* **24**, 1188 (1891).
425. König, J., *Chem.-Ztg.* **27**, 614 (1903); *Z. angew. Chem.* **25**, 654, 1545 (1912).
426. Simon, O., and Lorisch, H., *Z. physiol. Chem.* **42**, 56 (1904); **47**, 216 (1906).
427. Tollens, B., and Dmochowsky, R., *J. Landw.* **58**, 1 (1910).
428. Bühler, F. A., *Chem. Ind. (Berlin)* **26**, 138 (1903).
429. Councler, C., *Chem.-Ztg.* **24**, 369 (1900).
430. Klason, P., *Chem.-Ztg.* **27**, 585 (1903).
431. Klason, P., cf. E. Hägglund, in C. A. Schwalbe, *Die chemische Untersuchung pflanzlicher Rohstoffe etc.*, (Schriften d. Ver. d. Zellstoff- u. Papierchemiker, Berlin, Vol. 13, p. 129 (1920); *Svensk Papperstidn.* **27**, 262 (1924); *Papier-Fabr.* **22**, 373 (1924).
432. Hägglund, E., *Acta Acad. Aboensis, Math. et Phys.* **2**, No. 3 (1922).
433. Hägglund, E., and Klingstedt, F. W., *Cellulosechemie* **5**, 57 (1924). Cf. Hägglund, E., *Finnish Paper Timber J.* **4**, 444, 468 (1924).
434. Kalb, L., and Schoeller, V., *Cellulosechemie* **4**, 37 (1923).
435. Kürschner, K., and Hoffer, A., *Technol. u. Chem. Papier- u. Zellstoff-Fabr.* **26**, 125 (1929); **31**, 17 (1934).
436. Koslow, N. S., Oliphson, L. E., and Goldina, S. M., *Papier-Fabr.*, **35**, 46 (1937).
437. Wedekind, E., and Engel, O., German Pat. 581,806 (1933); *Zellstoff u. Papier* **13**, 557 (1933); *Ber.* **68**, 2363 (1935).
438. Kürschner, K., *Papier-Fabr.* **25**, 390 (1929).
439. Hägglund, E., *Svensk Papperstidn.* **31**, 572 (1928); Hägglund, E., and Proffe, B., *Svensk Kem. Tid.* **45**, 117 (1933).
440. Kullgren, C., *Svensk Kem. Tid.* **44**, 15 (1932).
441. Cf. Haar, A. W. van der, *Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren*, Berlin, 1920, p. 123.
442. Hägglund, E., *Svensk Papperstidn.* **31**, 572 (1928).
443. Staudinger, H., and Husemann, E., *Holz Roh- u. Werkstoff* **4**, 343 (1941).
444. Schmidt, E., and co-workers, *Ber.* **54**, 1860, 3241 (1921); **56**, 23 (1923); **57**, 1834 (1924); **58**, 1394 (1925); *Cellulosechemie* **12**, 62, 201 (1931).
445. Cf. Staudinger, H., and Jurisch, I., *Ber.* **71**, 2283 (1938).
446. Wan Chen, W.-H., and Cameron, F. K., *Ind. Eng. Chem.* **34**, 224 (1942).
447. Wise, L. E., Murphy, M., and D'Addieco, A. A., *Paper Trade J.* **122**, No. 2, 35 (1946).

448. Wise, L. E., and Ratcliff, E. K., *Ind. Eng. Chem., Anal. Ed.* **19**, 459 (1947).
449. Wise, L. E., Peterson, F. C., and Harlow, W. H., *Ind. Eng. Chem., Anal. Ed.* **11**, 18 (1939).
450. Bloom, T., and Jahn, E. C., *Tech. Ass. Papers* **24**, 127 (1941).
451. Jayme, G., and Schorning, P., *Papier-Fabr.* **36**, 235 (1938); **38**, 69 (1940).
452. Jayme, G., and Reh, F., *Cellulosechemie* **22**, 66 (1944).
453. Staudinger, H., and Husemann, E., *Holz Roh- u. Werkstoff* **4**, 345 (1941).
454. Klauditz, W., *Papier-Fabr.* **39**, 225 (1941).
455. Jayme, G., and Fink, F., *Cellulosechemie* **22**, 102 (1944).
456. Cundy, P. F., and Beck, M. M., *Paper Trade J.* **124**, No. 18, 36 (1947).
457. Schulze, E., *Ber.* **24**, 2285 (1891).
458. Cf. Pringsheim, H., Weinreb, K., and Karsten, E., *Ber.* **61**, 2025 (1928).
459. Cf., e.g., Schwalbe, C. G., *Z. angew. Chem.* **31**, 53 (1918).
460. Karrer, P., *Polymere Kohlenhydrate*, Leipzig, 1925, p. 263.
461. Staudinger, H., and Reinecke, F., *Holz Roh- u. Werkstoff* **2**, 321 (1939).
462. Candlin, E. J., and Schryver, S. B., *Proc. Roy. Soc. (London)* **B103**, 365 (1928).
463. Hawley, L. F., and Norman, A. G., *Ind. Eng. Chem.* **24**, 1190 (1932).
464. Cf. Heuser, E., and Merlau, O., *Cellulosechemie* **4**, 101 (1923).
465. Ritter, G. J., and Kurth, E. F., *Ind. Eng. Chem.* **25**, 1250 (1933); *J. Am. Chem. Soc.* **56**, 2720 (1934). Cf. Hägglund, E., and Ljungren, S., *Svensk Kem. Tid.* **46**, 83 (1934); Ritter, G. J., and Bird, C. D., *J. Am. Chem. Soc.* **59**, 802 (1937).
466. Jayme, G., *Papier-Fabr. Wochbl. Papierfabr.* **75**, 295 (1944).
467. Wise, L. E., *Paper Ind. and Paper World* **29**, 825 (1947).
- 467 a. Wise, L. E., *Pulp Paper Mag. Can.* **50**, 179 (1949).
468. Thomsen, Th., *J. prakt. Chem.* [2] **19**, 146 (1879).
469. Poumarède, J. A., and Figuier, L., *Compt. rend.* **23**, 918 (1846); **25**, 17 (1847).
470. Koch, F., *Ber.* **20**, 145 (1887).
471. Wheeler, H. J., and Tollens, B., *Ber.* **22**, 1046 (1889); *Ann.* **254**, 320 (1889).
472. Schorger, A. W., *Ind. Eng. Chem.* **16**, 142 (1924).
473. Cf. Salkowski, E., *Z. physiol. Chem.* **34**, 162 (1901); **35**, 240 (1902); Heuser, E., *J. prakt. Chem.* [2] **103**, 78 (1921).
474. Haworth, W. N., Hirst, E. L., and Oliver, E., *J. Chem. Soc.* **1934**, 1917; Voss, W., Bauer, R., and Pfirschke, J., *Ann.* **534**, 135 (1938).
475. O'Dwyer, M. H., *Biochem. J.* **20**, 656 (1926); Norman, A. G., *The Biochemistry of Cellulose*, Oxford, 1937, p. 53.
476. Freudenberg, K., Molter, H., and Dietrich, G., *Chem. Ber.* **80**, 53 (1947).
477. Stockman, L., and Hägglund, E., *Svensk Papperstidn.* **51**, 269 (1948).
478. Schmidt, E., and Graumann, E., *Ber.* **54**, 1867 (1921).
479. Schmidt, E., Tang, Y. C., and Jandebeur, W., *Cellulosechemie* **12**, 202 (1931).
480. Schmidt, E., Meinel, K., Jandebeur, W., and Simson, W., *Cellulosechemie* **13**, 138 (1932).
481. Voss, W., Bauer, R., Pfirschke, J., and Butter, G., *Angew. Chem.* **49**, 761 (1936); Voss, W., Bauer, R., and Pfirschke, J., *Ann.* **534**, 95 (1938).
482. Hess, K., and Lüdtke, M., *Ann.* **466**, 18 (1928).
483. Husemann, E., *J. prakt. Chem.* [2] **155**, 13 (1940).
484. Lüdtke, M., *Biochem. Z.* **268**, 372 (1934).
485. Preece, I. A., *Biochem. J.* **25**, 1304 (1931).
486. Norris, F. W., and Preece, I. A., *Biochem. J.* **24**, 59 (1930).
487. Voss, W., Bauer, R., and Pfirschke, J., *Ann.* **534**, 114 (1938).

488. Cf. Meyer, K. H., *Die hochpolymeren Verbindungen*, Leipzig, 1940, p. 329.
489. Klauditz, W., *Holz Roh- u. Werkstoff* **4**, 314 (1941).
490. Sisson, W. A., in Ott, E., *Cellulose and Cellulose Derivatives*, New York, 1943, p. 224.
491. Husemann, E., *J. prakt. Chem.* [2] **155**, 13, 64 (1940).
492. Dörr, R. E., *Papier-Fabr.* **39**, 273 (1941).
493. Hampton, H. A., Haworth, W. N., and Hirst, E. L., *J. Chem. Soc.* **1929**, 1739.
494. Haworth, W. N., and Percival, E. G. V., *J. Chem. Soc.* **1931**, 2850; Haworth, W. N., *Ber.* **65A**, 43 (1932); Haworth, W. N., Hirst, E. L., and Oliver, E., *J. Chem. Soc.* **1934**, 1917.
495. Schmidt, E., Meinel, K., Jandebeur, W., and Simson, W., *Cellulosechemie* **13**, 129 (1932).
496. Bywater, R. A. S., Haworth, W. N., Hirst, E. L., and Peat, S., *J. Chem. Soc.* **1937**, 1983.
497. Staudinger, H., and Husemann, E., *Ann.* **527**, 195 (1937).
498. Husemann, E., *J. prakt. Chem.* [2] **155**, 13 (1940).
- 498 a. Wise, L. E., and Rittenhouse, R. C., *Tappi* **32**, 397 (1949).
- 498 b. Erdtman, H., *Svensk Papperstidn.* **46**, 226 (1928); *Tappi* **32**, 305 (1949).
- 498 c. Anderson, A. B., and Erdtman, H., *J. Am. Chem. Soc.* **71**, 2927 (1949).
499. Cf. particularly: Hägglund, E., and Klingstedt, F. W., *Cellulosechemie* **5**, 57 (1924); Klingstedt, F. W., *Z. anal. Chem.* **66**, 129 (1925); Gierisch, W., *Cellulosechemie* **6**, 61 (1925).
500. Kullgren, C., and Tydén, H., *Ing. Vetenskaps Akad. Handl.* No. 94 (1929).
501. Öman, E., *Svensk Kem. Tid.* **36**, 19 (1924).
502. Hughes, E. F., and Acree, S. F., *J. Research Natl. Bur. Standards* **2**, 327 (1938).
503. Cf. Howells, H. P., *Papier-Fabr.* **35**, 25 (1937); Gierisch, W., *Cellulosechemie* **6**, 61 (1925).
504. Pervier, N. C., and Gortner, R. A., *Ind. Eng. Chem.* **15**, 1167, 1255 (1923); Powell, W. J., and Whittaker, H., *J. Soc. Chem. Ind. London* **43**, 35 (1924); Hughes, E. F., and Acree, S. F., *Ind. Eng. Chem., Anal. Ed.* **26**, 123 (1934), *J. Research Natl. Bur. Standards* **24**, 175 (1940).
505. Schmidt, E., Meinel, K., Nevros, K., and Jandebeur, W., *Cellulosechemie* **11**, 61 (1930).
506. Hägglund, E., and Rosenqvist, T., *Biochem. Z.* **179**, 376 (1926).
507. For references see *Papier-Fabr.* **23**, 226 (1935).
508. Lechner, R., *Z. Spiritusind.* **63**, 167 (1940).
509. Stillings, R. A., and Browning, B. L., *Ind. Eng. Chem., Anal. Ed.* **12**, 499 (1940).
510. Fleury, P., and Poirots, G., *J. pharm. chim.* [7], **26**, 87 (1922); Pedinelli, M., and Pessarelli, V., *Boll. sci. facolta chim. ind., Bologna* **1940**, 99.
511. Cf. Svenska Pappers- och Cellulosaingenjörsföreningens tekniska meddelanden. CCA 25; *Svensk Papperstidn.*, in press.
512. Jayme, G., and Sarten, P., *Biochem. Z.* **308**, 109, (1941).
513. Bertrand, G., *Compt. rend.* **129**, 1027 (1899).
514. Tollens, B., *Ber.* **22**, 1046 (1889).
515. Hess, K., and Lüdtke, M., *Ann.* **466**, 18 (1928).
516. Hess, K., and Lüdtke, M., *Ber.* **61**, 465 (1928).
517. Lenze, F., Pleus, B., and Müller, J., *J. prakt. Chem.* [2] **101**, 213 (1921).
518. Schorger, A. W., *Ind. Eng. Chem.* **9**, 748 (1917).
519. Hägglund, E., *Holzchemie*, 1st ed., Leipzig, 1928, p. 78.

520. Nowotownna, A., *Biochem. J.* **30**, 2177 (1936).
521. Norman, A. G., and Jenkins, S. H., *Biochem. J.* **27**, 818 (1933).
522. Hägglund, E., and Bratt, L. C., *Svensk Kem. Tid.* **43**, 125 (1936); cf. also Hägglund, E., and Klingstedt, F. W., *Cellulosechemie* **5**, 57 (1924); **9**, 77 (1928); Hägglund, E., and Proffe, B., *Svensk Kem. Tid.* **45**, 117 (1933).
523. Koch, H., *Papier-Fabr.* **38**, 66 (1940); *ibid.*, **39**, 46 (1941).
524. Dore, W. H., *J. Ind. Eng. Chem.* **12**, 476 (1920).
525. Unpublished.
526. Hägglund, E., and Larson, R., *Svensk Papperstidn.* **44**, 477 (1941).
527. Haar, A. W. van der, *Anleitung zum Nachweis, zur Trennung und Bestimmung der Monosaccharide und Aldehydsäuren*, Berlin, 1920.
528. Svenska Pappers- och Cellulosaingeniörsfören. tekn. meddel., CCA 4, *Svensk Papperstidn.* **46**, 587 (1943); Jayme, G., and Sarten, P., *Biochem. Z.* **303**, 114, (1941).
529. Menzinsky, G., *Svensk Papperstidn.* **45**, 421 (1942).
530. Cf. Schmidt, E., Atterer, M., and Schnegg, H., *Cellulosechemie* **10**, 127 (1929).
531. Hess, K., Lüdtke, M., and Rein, H., *Ann.* **466**, 58 (1928).
532. Jayme, G., and Hanke, G., *Cellulosechemie* **21**, 127 (1943); Jayme, G., and Fink, F., *Cellulosechemie* **22**, 102 (1944).
533. Müller, O., *Ann.* **553**, 81, 157 (1947).
534. Tollens, B., and Lindsey, J. B., *Ann.* **267**, 341 (1891); Krause, H., *Chem. Ind. Berlin* **29**, 217 (1906); Hägglund, E., *Biochem. Z.* **70**, 416 (1915); Klason, P., *Kempe-Festschrift, Skogsvårdsföreningens Tid.* **15**, 224 (1917).
535. Hägglund, E., and Klingstedt, F. W., *Cellulosechemie* **5**, 57 (1924).
536. Schorger, A. W., and Smith, D. F., *Ind. Eng. Chem.* **8**, 494 (1916).
537. Hägglund, E., unpublished.
538. Dore, W. H., *Ind. Eng. Chem.* **12**, 477 (1920).
539. Wise, L. E., and Peterson, F. C., *Ind. Eng. Chem.* **22**, 362 (1930); Wise, L. E., Hamer, P. L., and Peterson, F. C., *ibid.* **25**, 184 (1933); Peterson, F. C., Maughan, M., and Wise, L. E., *Cellulosechemie* **15**, 109 (1934); Wise, L. E., and Unkauf, H., *ibid.* **14**, 20 (1933).
540. Peterson, F. C., Barry, A. J., Unkauf, H., and Wise, L. E., *J. Am. Chem. Soc.* **62**, 2361 (1940).
541. Hirst, E. L., Jones, J. K. N., and Campbell, W. G., *Nature* **147**, 25 (1941).
542. White, E. V., *J. Am. Chem. Soc.* **63**, 2871 (1941); **64**, 302, 1507 (1942).
543. König, J., and Becker, E., *Z. angew. Chem.* **32**, 155 (1919). Cf. Fromherz, K., *Z. physiol. Chem.* **50**, 238 (1906); O'Dwyer, M. H., *Biochem. J.* **17**, 501 (1923).
544. Schmidt, E., Atterer, M., and Schnegg, H., *Cellulosechemie* **10**, 126 (1929). Cf. Schmidt, E., Atterer, M., and Thaler, H., *Cellulosechemie* **10**, 153 (1929).
545. Kurth, E. F., and Ritter, G. J., *J. Am. Chem. Soc.* **56**, 2720 (1934).
546. Wise, L. E., and Appling, J. W., *Ind. Eng. Chem., Anal. Ed.* **16**, 28 (1944).
547. Brauns, F. E., *Science* **102**, 155 (1945).
548. Sherrard, E. C., and Blanco, G. W., *Ind. Eng. Chem.* **15**, 611 (1923). Cf. Kurth, E. F., and Ritter, G. J., *J. Am. Chem. Soc.* **56**, 2722 (1934).
- 548 a. Sundman, J., Dissertation, Meddelanden från Industrins Centrallaboratorium **71**, Helsingfors, 1949.
- 548 b. Sundman, J., *Paper and Timber (Finland)* **32**, 306 (1950).
549. Ehrlich, F., *Chem.-Ztg.* **41**, 197 (1917); *Biochem. Z.* **168**, 263 (1926).

550. Henglein, F. A., *J. makromol. Chem.* **1**, 128 (1943). Cf. concerning pectin: Norman, A. G., *The Biochemistry of Cellulose*, Oxford, 1937; Meyer, K. H., *Natural and Synthetic High Polymers*, New York, 1942; Schneider, G. G., and Bock, H., *Ber.* **70**, 1617 (1937); Speiser, R., Eddy, C. R., and Hills, C. H., *J. Phys. Chem.* **49**, 563 (1945); Speiser, R., and Eddy, C. R., *J. Am. Chem. Soc.* **68**, 287 (1946).
551. Fellenberg, Th. v., *Biochem. Z.* **85**, 45 (1918).
552. Schwalbe, C. G., and Becker, E., *Z. angew. Chem.* **32**, 229 (1919).
553. Mehta, M. M., *Biochem. J.* **19**, 969 (1925).
554. Ritter, G. J., *Ind. Eng. Chem.* **17**, 1194 (1925).
555. Hägglund, E., Klingstedt, F. W., Rosenqvist, T., and Urban, H., *Z. physiol. Chem.* **177**, 248 (1928).
556. Schwalbe, C. G., and Feldtmann, G. A., *Ber.* **58**, 1534 (1925).
557. O'Dwyer, M. H., *Biochem. J.* **17**, 501 (1923).
558. O'Dwyer, M. H., *Biochem. J.* **20**, 656 (1926).
559. Norman, A. G., and Norris, F. W., *Biochem. J.* **24**, 402 (1930); Norris, F. W., and Preece, I. A., *Biochem. J.* **25**, 1304 (1931); Ritter, G. J., and Mitchell, R. L., *J. Am. Chem. Soc.* **62**, 1958 (1940).
560. O'Dwyer, M. H., *Biochem. J.* **33**, 713 (1939).
561. Rogers, S. C., Mitchell, R. L., and Ritter, G. J., *Ind. Eng. Chem., Anal. Ed.* **19**, 1029 (1947).
562. Wurz, O., *Papier-Fabr.* **35**, 185 (1937).
- 562 a. Sohn, A. W., *Ber.* **82**, 230 (1949).
- 562 b. Sohn, A. W., and Lenel, P. O., *Das Papier* **3**, 109 (1949).
563. Krause, H., *Chem. Ind. Berlin* **29**, 217 (1906).
564. Hägglund, E., *Biochem. Z.* **70**, 416 (1915).
565. Klason, P., *Skogsvårdsföreningens Tid.* **13**, 224 (1915); Klason, P., *Kempe-Festschrift, Skogsvårdsföreningens Tid.* **15**, 224 (1917).
566. Höpner, Th., *Cellulosechemie* **22**, 33 (1944).
567. Sundman, J., *Finnish Paper Timber J.* **29**, 113 (1947).
568. König, J., and Becker, E., *Z. angew. Chem.* **32**, 155 (1919).
569. Sherrard, E. C., and Blanco, W. G., *Ind. Eng. Chem.* **15**, 611 (1923).
570. Sherrard, E. C., and Blanco, W. G., *Ind. Eng. Chem.* **15**, 1166 (1923).
571. Hägglund, E., *Holzchemie*, 2nd ed., Leipzig, 1939, p. 121.
572. Hägglund, E., *Finnish Paper Timber J.* **4**, 444 (1924).
573. Klason, P., *Kempe-Festschrift, Skogsvårdsföreningens Tid.* **15**, 217 (1917).
574. Hägglund, E., *Holzchemie*, 2nd ed., Leipzig, 1939, p. 122.
575. Hägglund, E., *Ber.* **56**, 1866 (1923); Hägglund, E., *Cellulosechemie* **4**, 77 (1924).
- 575 a. Sundman, J., Saarnio, J., and Gustafsson, C., *Finnish Paper Timber J.* **31**, 467 (1949).
576. Browne, C. A. jr., and Tollens, B., *Ber.* **35**, 1466 (1902); Hauers, R., and Tollens, B., *Ber.* **36**, 3319 (1903). Cf. O'Dwyer, M. H., *Biochem. J.* **17**, 501 (1923).
577. Chalmot, G. de, *J. Am. Chem. Soc.* **16**, 218 (1894).
578. Schorger, A. W., *Ind. Eng. Chem.* **9**, 556 (1917).
579. Mahood, S. A., and Cable, D. E., *Ind. Eng. Chem.* **14**, 933 (1922).
580. Ritter, G. J., and Fleck, L. C., *Ind. Eng. Chem.* **14**, 1050 (1922).
581. Ritter, G. J., and Fleck, L. C., *Ind. Eng. Chem.* **15**, 1005 (1923); **18**, 576 (1926).
582. Hägglund, E., Sandelin, O., Nyman, C., Eriksson, T., and Koskull, H. v., *Svensk Papperstidn.* **37**, 133 (1934); Hägglund, E., *Papier-Fabr.* **33**, 73 (1935).

583. Häggglund, E., Ljunggren, S., Nihlén, H., and Sandelin, O., *Svensk Papperstidn.* **38**, 454 (1935).
584. Häggglund, E., *Holzchemie*, 2nd ed., Leipzig, 1939, p. 125.
585. Häggglund, E., and Johnson, T., *Finnish Paper Timber J.* **6**, 524 (1926).
586. Cross, C. F., Bevan, E. J., and Beadle, C., *Ber.* **26**, 2520 (1893); **27**, 1061, 1456; **28**, 2604 (1895).
587. Cross, C. F., Bevan, E. J., and Smith, C., *J. Chem. Soc.* **69**, 804 (1896); **71**, 1001 (1897). Cf. Smith, C., *Proc. Chem. Soc.* **10**, 89 (1894).
588. Cross, C. F., and Bevan, E. J., *J. Chem. Soc.* **113**, 182 (1918).
589. Heuser, E., and Haug, A., *Z. angew. Chem.* **31**, 166 (1918); Irvine, J. C., and Hirst, E. L., *J. Chem. Soc.* **125**, 15 (1924).

CHAPTER III

IV. Lignin

A. INTRODUCTION. COLOR REACTIONS OF WOOD.

The first investigations of the elementary composition of wood were made by J. L. Gay-Lussac and L. J. Thenard (1) as early as the beginning of the last century. These investigations were later extended to a large number of materials (2), and, as has already been mentioned above, great similarities were found in the elementary compositions of different woods. The view was long held that wood was a homogeneous substance, rather than a mixture of various substances. The experiments of A. Payen (3) showed that wood membranes did not consist of pure cellulose. By treating lignified tissues with nitric acid and alkali, he succeeded fairly well in isolating and identifying more or less pure cellulose. It was necessary to remove the "incrusting substances" in order to lay the cellulose bare. F. Schulze (4) found that a mixture of nitric acid and potassium chlorate was suitable for this purpose. He designated the substance which was easily destroyed by this reagent as *lignin*. We now know that Schulze's mixture dissolves not only the substance which is now usually called lignin, but also large amounts of carbohydrates, consisting mostly of wood polyoses. Schulze's formula for lignin has, therefore, among other things, far too little carbon. As these facts became known, the concept of lignin gradually narrowed, and the opinion is generally held today that a pure lignin must not contain any residues which are capable of conversion to sugar. Complete unanimity on this point has, however, not yet been achieved. E. Schmidt and his co-workers, for example, were of the opinion that the lignin consists of constituents of the wood which are attacked by chlorine dioxide, whereas the "skeletal substance" is not attacked (5). This reagent dissolves not only the lignin, in its narrower sense, but also considerable quantities of carbohydrates, especially pentosans. This mixture is to be regarded as the "incrusting material" (6).

Investigations of straw and of beech wood have led R. S. Hilpert and his co-workers (7) to the conclusion that there is no fundamental difference between lignin and the carbohydrates present in these materials. On the one hand, these authors assert that the lignin cannot be determined by treatment with strong acids, as has hitherto been customary. Treatment

with these reagents for long periods of time results in more or less degradation of the carbohydrates to humus-like materials (8), which are therefore determined as lignin. On the other hand, it was found during the lignin determinations on straw that the quantity of residue remaining undissolved after acid hydrolysis depended very greatly on the temperature. At -10°C , for example, only 15-20 % as much lignin was found as at room temperature. According to Hilpert, the material going into solution consists of a dehydrated cellulose, or in other words, a cellulose anhydride. According to this point of view, the material which is usually designated as lignin is nothing more than acid-insoluble *reaction products*, and is not to be considered as a component of the wood. F. Schütz and P. Sarten (9) are of the same opinion. They allowed aromatic diazo compounds to act upon wood, for they thought that if the lignin were present in the form of phenols, they would give the usual azo dyes. Such dyes could not be isolated, however. These authors also found that a large part of the wood could be dissolved by superheated steam, and that the dissolved material had the same composition as the original wood.

This last fact was established by noting that the residue had the same composition as the original wood. A substance could be precipitated from the aqueous extract; they assumed that this was lignin.

F. Schütz (10) has later combined the steam extraction of wood with a hydrogen-peroxide oxidation. The fact that the wood then gradually goes completely into solution, without any change in the composition of the residue during the course of the reaction is taken by Schütz to be a strong support for his theory that wood is a uniform chemical substance. This theory, which is also shared to a limited extent by R. Hilpert (11) is, however, by no means established, and is in obvious disagreement with many facts. In this connection mention may be made of P. W. Lange's proof (12) of the aromatic nature of native lignin, by means of ultraviolet spectrography (cf. p. 294 and 424). A. Frey-Wyssling (13) and K. Hess (14) as well as G. Jayme (14 a) have come out against the theory of Schütz, partly on botanical grounds, partly on the basis of chemical arguments.

It is in any case certain that lignin can not be defined as a component of wood which is under all circumstances insoluble in strong mineral acids. This had already been recognized (15).

It was early discovered that lignified membranes showed characteristic *color reactions* with certain organic reagents. F. F. Runge (16) was probably the first to investigate this matter. He found that spruce wood was colored blue by phenol in hydrochloric acid solution, while wood treated with aniline sulfate gave a yellow color. Many other investigators, mostly

botanists, later described the reactions of wood with other phenols and aromatic amines, as well as other organic bases. The following examples may be cited:¹

Reagent	Color	Author
Aniline.....	Yellow	F. F. Runge (16)
o-, m-, and p-chloroaniline.....	Orange-yellow	E. Covelli (17)
o-, and p-aminophenol.....	Orange-yellow	E. Covelli (17)
Dimethyl-p-phenylenediamine.....	Red	C. Wurster (18)
Benzidine.....	Red-yellow	S. Dukelsky (19)
Pyrrole.....	Red	A. Ihl (20)
Phenol.....	Greenish-blue	F. F. Runge (16)
Guaiaicol.....	Yellow-green	F. Czapek (21)
Phloroglucinol.....	Violet-red	J. v. Wiesner (22)
Orcinol.....	Dark red	E. O. v. Lippmann (22)

The question as to what substances in the wood caused the color reactions has naturally been much discussed. E. Nickel found (23) that wood which had been treated with sodium bisulfite no longer gave a reaction with aniline sulfate. Wood was also found to behave like an aldehyde toward fuchsin-sulfurous acid solutions. It was assumed that the aldehydic properties were to be attributed to the lignin, and that the lignin formed compounds with primary and secondary amines. Tertiary amines do not react.

F. Czapek (24), however, later thought that he had found that the color reactions were due to a substance "hadromal", which is present in wood in small quantities, and which is liberated by treating wood meal with stannous chloride solution at 75°C. The substance was obtained in yields of 1-2 % of the weight of the wood by extracting the resulting solution with benzene.

After purification it melted at 75-80°C. It showed aldehydic and phenolic properties. It was assumed that this substance was chemically combined with the carbohydrate of the wood, and that the bond was broken by the hydrolytic action of the stannous chloride. Hadromal gave the same color reactions as the wood. Czapek (25) later expressed the opinion that hadromal was closely related to coniferyl alcohol, and that most of it was present in wood as esters of cellulose and other carbohydrates.

V. Grafe (26) has contested Czapek's view that hadromal is a uniform substance; he could hardly prove this point, however, since he carried out the extraction at 180°C with water or hydrochloric acid, instead of following the directions of Czapek. Under the conditions used by Grafe a mixture of pyrocatechol, vanillin, and methylfurfural was formed.

A new, intensive investigation of hadromal was later undertaken by C. Hoffmeister (27). In contrast to Grafe, he confirmed the results of

¹ For further examples see M. Phillips, in L. E. Wise, *Wood Chemistry*, New York, 1946, p. 277-278.

Czapek. Careful treatment of wood with stannous chloride, and subsequent extraction with benzene yielded a crystalline substance with the formula $C_{10}H_{10}O_3$ melting at 86°C and giving an immediate red-violet precipitate with phloroglucinol in hydrochloric acid.

Hoffmeister believed this product to be identical with coniferaldehyde. Somewhat later, Pauly and Feuerstein (28) criticized sharply Hoffmeister's work and stated that hadromal did not contain any trace of coniferaldehyde. From the data given by Hoffmeister, they concluded that his hadromal consisted essentially of vanillin. In accordance herewith, Wiechert (29) came to the result that hadromal from beech wood was not identical with coniferaldehyde.

This problem has recently been solved by the isolation of both coniferaldehyde and vanillin as 2,4-dinitrophenylhydrazones from (spruce) hadromal preparations [E. Adler and L. Ellmer (30)]. By a comparison of the absorption spectra of the colors obtained from hadromal solutions with phloroglucinol-HCl or with aromatic amines and the corresponding colors produced by pure coniferaldehyde it could be definitely established that this aldehyde is responsible for the color reactions of hadromal. The coniferaldehyde content of hadromal preparations was measured spectrophotometrically. It amounted to only 0.02 % of the wood weight. The yield of vanillin was approximately 0.05 %.

The suggestion was early advanced that lignin might be determined colorimetrically, on the basis of the red color given by wood with phloroglucinol and hydrochloric acid (31). F. Czapek (32) raised the objection that such a method would at best give only a hadromal determination, and not one of the lignin. There are certain plant membranes which give the same phloroglucinol reaction as wood, although they are, strictly speaking, not lignified. Therefore, such a method could not be applied with unambiguous results.

An interesting study of the reactions of wood with phloroglucinol and with aromatic amines is due to C. F. Cross and his co-workers (33). They found, that only small amounts of the phenol are taken up to form the colored material, but that a combination of the phenol with the wood also occurs, causing large amounts of phenol to enter into a reaction of another kind.

Substance	Amount of Phloroglucinol Taken Up, in % of the Substance
Mechanical pulp from softwood	6.71-6.63
Jute fiber.....	4.23-4.34
Sulfite pulp.....	0.75
Esparto pulp.....	0.5
Cotton cellulose.....	0.2

If jute was chlorinated or acetylated, no color reaction occurred, but

phloroglucinol was nevertheless taken up. The authors conclude from this that the lignin complex is not affected by chlorination or acetylation. This would indicate that the main phenol reaction depends on the presence of a quinone group rather than an aldehyde; the aldehyde group would, however, be characteristic of the substance which gives the typical color reaction of the wood.

E. Ungar (34) has doubted the finding of Cross and his co-workers, that spruce wood takes up a constant quantity of phloroglucinol. Ungar thinks that this quantity depends on the reaction conditions, especially the concentrations of phloroglucinol and of hydrochloric acid.

The red-violet color given by wood with phloroglucinol and hydrochloric acid has been erroneously identified with the well-known pentosan reaction (35); the latter occurs only at elevated temperatures, while the phloroglucinol color develops fully even in the cold.

The opinion was early expressed that the condensation between wood and phloroglucinol or other phenols is a carbonyl reaction (36). W. Fuchs (37) thought that in the case of the color reactions with phenols, the *para*-position of the phenol nucleus was the site of condensation. K. G. Jonas (38) believed that the dissolution of lignin by phenols is also due to a condensation between the carbonyl of the lignin and the *para*-position of the phenol (concerning the formation of "phenol lignins" cf. p. 246).

As for the color reactions of wood with amines and other organic bases, the view as to the mechanism diverged widely. The reaction was attributed by some to the lignin and by others to the trace materials in the wood. Dimethyl-*p*-phenylenediamine has been used for the quantitative determination of lignin. C. F. Cross and his co-workers (33) investigated the amounts of this reagent taken up by mechanical pulp as increasing quantities of the amine were added. Four 1 g. samples of air-dry wood were treated respectively with 0.005, 0.01, 0.02, and 0.05 g. of the amine hydrochloride, dissolved in 20 cc. of 5 % sodium acetate. The intensity of the color was found to increase proportionately to the amount of base added. After 16 hours all the samples still contained an excess of base. Nitrogen determinations of the wood revealed that the following quantities of amine had been taken up:

Quantity of Amine Hydrochloride Used, %	Quantity of Amine Taken Up, %
0.5	0.14
1.0	0.28
2.0	0.56
5.0	2.45

Cross believed that these results demonstrated that the reaction depends

on the presence of aldehyde groups in the "lignocellulose" or its accessory components. He also believed that the reaction is an adsorption process, since an equilibrium appeared to exist between the lignocellulose-amine compound and the free base.

Such an equilibrium did not exist in the case of phenylhydrazine, for all of the phenylhydrazine added reacted, according to these authors, when the concentration of the base was low. It was assumed that the reactive groups were the same as those in the case of phloroglucinol.

At higher temperatures and in the presence of acid catalysts the lignin of wood combines with larger amounts of amines. P. Klason (39), for example, found that when softwood was heated for 24 hours to 100° C with 0.1 *N* hydrochloric acid, it took up as much naphthylamine as one would expect it to do, on the assumption that each molecule of lignin combined with one molecule of naphthylamine. It was even possible to base a quantitative determination of lignin on this reaction.

The results of Klason were confirmed by E. Hägglund and T. Johnson (40), who also found that this was not an adsorption; 100 g. of extracted spruce wood took up 11.5 g. of naphthylamine and 10.3 g. of guaiacol, or, in other words, the same number of equivalents of the two reactants.

K. Hess and K. E. Heumann (41), using winter rye straw which had been disintegrated in an oscillating beater, succeeded in obtaining 13 % of the material in the form of a lignin-hydrazine compound. (Cf. p. 254).

These results, interesting as they are, do not permit one to draw any certain conclusions as to whether the color reactions of wood with phenols and amines are due to the lignin or to traces of other materials.

L. Zechmeister (42) studied the reaction of wood with amines and concluded that the reactive group in wood is an aromatic aldehyde, present only in small amounts and bound to a larger group. The larger group was assumed to be a carbohydrate — a "cellulose component." These conclusions were based on the similarities in the behavior toward aniline of the "wood aldehyde" and the aldehydic glucosides like helicin and vanillin glucoside. The anilides of aldehydic glucosides show much the same color-stability toward ether and hydrochloric acid as does that of the wood aldehyde; aromatic anilides are different.

Zechmeister's results were later confirmed by E. Ungar (34), who worked in Willstätter's laboratory. Only small amounts of aniline (2.32 %) were taken up, even when the reagent was used in great excess. This was also true for hydroxylamine and semicarbazide. If the aldehyde groups were blocked with these reagents, the wood no longer gave any color reactions. If the aldehyde groups were destroyed by oxidation with perbenzoic acid no aniline was taken up (43).

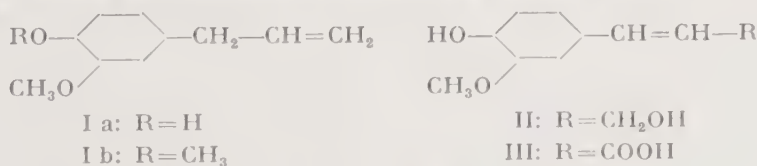
E. C. Crocker (11) expressed the opinion, that the phloroglucinol reaction is due to traces of a single aldehyde accompanying the lignin rather than to any group in the lignin molecule itself. He suggested that the aldehyde was coniferaldehyde.

It has long been assumed that besides the hadromal, cinnamaldehyde is the substance in the wood which gives the phloroglucinol reaction, for cinnamaldehyde likewise gives a red color with this reagent (45). P. Klason (46) was for a time of the same opinion. It should be pointed out, however, that the color produced by cinnamaldehyde is brownish-red and not violet-red as is the color obtained with wood.

Vanillin was also long thought to take part in the color reactions, along with the cinnamaldehyde; this viewpoint was first advanced by M. Singer (17, 26), and has since found many adherents. O. Richter (48), among others, has cited the phloroglucinol reaction as an experimental confirmation of the fact that the color reactions of wood are due to the presence of vanillin. E. Nickel (23) and T. Seliwanoff (49) have contested this. As a matter of fact, vanillin gives only a pale pink color under conditions which produce a strongly violet-red color with wood or with coniferaldehyde (see p. 188).

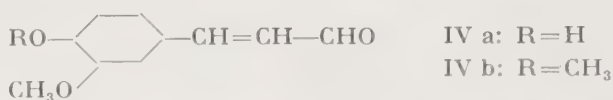
K. Freudenberg (50) believed that the characteristic lignin reaction—red coloring with phloroglucinol and hydrochloric acid—is quite unspecific, since it is given by a wide variety of hydroxy and methoxy benzene derivatives with unsaturated side chains.

This assumption was in accordance with the results of F. Czapek (21), who had stated that substances like eugenol (I a), eugenol methyl ether (I b), coniferyl alcohol (II) and ferulic acid (III) give red color reactions with phloroglucinol-hydrochloric acid, similar to those of wood.



The opinion that coniferyl alcohol (II) gives a positive phloroglucinol reaction, was also maintained by K. Kürschner (51), who believed that it was this substance which caused the color reactions of wood. P. Klason (52) has, however, clearly demonstrated that coniferyl alcohol does not give any color reaction with phloroglucinol-HCl, and that this reaction becomes positive only on mild oxidation of the alcohol, probably by formation of coniferaldehyde. Czapek's statement, that ferulic acid (III) gives a positive reaction with phloroglucinol, is likewise erroneous, as has been shown by E. Adler, K. J. Björkqvist, and S. Häggroth (53).

Several authors came, in accordance to Czapek, to the result, that eugenol (I a) and eugenol methyl ether (I b), give the characteristic red-violet color with phloroglucinol-hydrochloric acid (54, 55, 56). Podbreznik (55) stated that the color reactions produced by eugenol approached most closely those of lignin. A reinvestigation of this question carried out by E. Adler, K. J. Björkqvist and S. Häggroth (53) showed, however, that this view is wrong. Eugenol and its methyl ether, purified by a careful fractional distillation, do not give the phloroglucinol reaction; on standing, however, a phloroglucinol-reactive impurity develops in the distilled samples. The phloroglucinol reaction in crude preparations of eugenol and eugenol methyl ether is therefore caused by some impurity. This could be identified as coniferaldehyde (IV a) and its methyl ether (IV b), respectively.

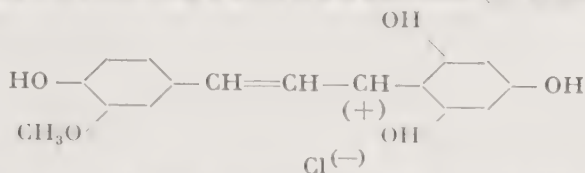


The presence of analogous unsaturated aldehydes in samples of other allyl substituted aromatic compounds has also been demonstrated.

From these results it appears that the phloroglucinol reaction is of a much greater specificity than was formerly believed. First of all, it seems to be quite certain that the phloroglucinol-reactive substances are aldehydes. This is in accordance with the fact, that pretreatment of wood with carbonyl reagents like hydroxylamine and semicarbazide [Seliwanoff (57), Ungar (34)] as well as with the specific aldehyde reagent dimedone (E. Adler, unpublished) inhibits the color reactions. Furthermore, barbituric acid, which forms colored condensation products with aldehydes (58, 59), also gives an orange yellow color with wood [Pavolini (60)] as well as with certain isolated lignin preparations and with coniferaldehyde (E. Adler, unpublished).

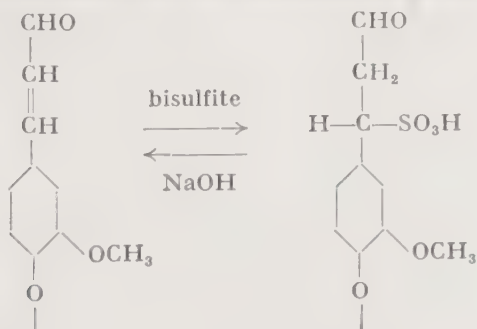
Regarding the constitution of the phloroglucinol-reactive aldehyde it has already been mentioned that aromatic aldehydes like vanillin and veratraldehyde give only faint pink colors, while cinnamaldehyde yields a red-brown color. By substituting the benzene nucleus in the latter substance with hydroxyl and methoxyl groups one obtains coniferaldehyde and its methyl ether, which at present are the only substances known to give phloroglucinol reactions of approximately the same quality as those obtained with wood and certain isolated lignin preparations. The same is true for the color reactions with other phenols and with aromatic amines. These arguments, together with the fact that coniferaldehyde has been isolated from wood (cf. page 184), constitute extremely strong evidence that coniferaldehyde groups are responsible for the color reactions of wood.

As to the constitution of the colored reaction products between coniferylaldehyde and phenols, as for instance phloroglucinol, in the presence of strong acids, the following structure is assumed (E. Adler, unpublished):



As mentioned above, the question as to whether the color producing aldehyde is a low-molecular trace substance, occurring in a free state in the wood or in some way bound to the carbohydrate constituents of the wood, or whether it is a part of the lignin macromolecule, has been answered in different ways by different authors. Recently, definite proof has been furnished that coniferaldehyde groups are a part of the lignin molecule. According to F. E. Brauns (61) (cf. page 194), the so-called "native lignin," an alcohol-soluble lignin fraction, gives the typical phloroglucinol reaction. It has been found, that the absorption spectrum of the red-violet color obtained agrees well with that obtained from coniferaldehyde (53). The "native lignin" of Brauns represents, however, only a few per cent of the total lignin content of the wood. The presence of coniferaldehyde groups in the bulk of the lignin has been shown indirectly by E. Adler and co-workers (53, 30) who have demonstrated the occurrence of such groups in liginosulfonic acid. The original liginosulfonic acids, such as can be separated from sulfite waste liquors, give no phloroglucinol reaction, or only a weak one. It was then found that solutions of liginosulfonic acid will show a strong phloroglucinol reaction, if they are pretreated with alkali for a few minutes at room temperature. This effect is explained in the following way:

Coniferaldehyde groups, contained in the original lignin molecules, are converted, during the sulfite cook, into the corresponding hydrosulfonic acid derivative. From this, bisulfite is readily split off on gentle alkaline treatment ("loosely bound" sulfite, cf. Chapter V, page 430), and the phloroglucinol-reactive coniferaldehyde group is regenerated:



The existence of the reactions represented in this scheme was clearly demonstrated in model experiments, in which free coniferaldehyde and its corresponding hydrosulfonic acid were used.

By spectrophotometric comparison with pure coniferaldehyde, the amount of coniferaldehyde groups in lignosulfonic acid could be estimated. In lignosulfonic acids, obtained from hard pulp waste liquors, there was one coniferaldehyde group for each 40-50 OCH_3 groups. Approximately the same ratio was computed for the original lignin in spruce wood (30) on the basis of colorimetric studies.

It seems reasonable to assume that the coniferaldehyde groups constitute end groups of the lignin molecules.

The total amount of coniferaldehyde groups in wood is approximately 0.5 per cent. However, only a small fraction of this, about 0.02 % of the wood weight, has been found in a free state in the hadromal preparations (cf. page 184).

Additional proof of the existence of (sulfonated) coniferaldehyde groups in lignosulfonic acids has been furnished by the following experiments (61 a):

Free coniferaldehyde as well as the corresponding hydrosulfonic acid are easily decomposed to acetaldehyde and vanillin in boiling 0.1 N NaOH (cf. page 233). It was then found that under similar conditions acetaldehyde was also liberated from lignosulfonic acids. As the acetaldehyde was liberated, the amount of coniferaldehyde groups in the solution, measured colorimetrically after addition of phloroglucinol-HCl, decreased and the acetaldehyde formation ceased when coniferaldehyde groups could no longer be detected.

Besides the organic compounds mentioned above, various *inorganic reagents for wood* have also been proposed.

C. F. Cross and E. J. Bevan (62) found that fibers containing lignin gave a deep greenish-blue color on treatment with a liquid prepared by mixing ferric chloride and freshly prepared potassium ferrieyanide solutions. This reaction is not specific for wood; the color is also given by other reducing agents.

The reaction with chlorine is more characteristic. A. Payen (63) was the first to find that wood was colored red when it was treated first with chlorine and then with ammonia. Chlorine is bound to the fibers, giving no color if it is dry, but an intense yellow if it is moist. When the chlorinated wood is treated with sodium sulfite solution, the color changes to red (64). This reaction is quite specific for lignin. It was assumed that the chlorination product is a chloroquinone, which is related to pyrogallol, but strong doubts have been expressed about this (65).

It has also long been known that wood is colored green by hydrohalic acids (26). A strong yellow color appears before the green develops. E. Ungar (34) found that this color reaction is inhibited by pretreating the wood with hydroxylamine, similar to the color reactions with phenols and amines. F. E. Brauns (61) found that the alcohol-soluble "native lignin" was colored an intense green in hydrochloric acid.

Examination of a great number of model substances by E. Adler, K. J. Björkqvist and S. Häggroth (53) revealed that only coniferaldehyde and coniferaldehyde methyl ether showed the color reaction with concentrated hydrochloric acid (yellow to green), which is characteristic for wood. This indicates, that the same group (of coniferaldehyde type) in the lignin is responsible for the color reactions with phenols and aromatic amines as well as with concentrated hydrochloric acid.

Sulfuric acid of about 75 per cent concentration also gives the yellow-green color reaction with wood or coniferaldehyde.

If wood is preheated with sulfite solutions, no yellow-to-green color reaction is obtained. This result is similar to that known from the color reactions with phenols and aromatic amines. The reason for this inhibition is, of course, that bisulfite is added to the double bond of the coniferaldehyde side chains in lignin. This is proved by the fact that a short treatment of the sulfite-cooked wood with dilute alkali at room temperature makes the color reaction with concentrated hydrochloric acid or strong sulfuric acid reappear, which is in complete analogy to the behavior of sulfite-cooked wood with respect to its color reactions with phenols and aromatic amines (E. Adler, unpublished, cf. p. 189). F. A. Abadie (65 a), who obviously was not aware of these facts, erroneously believed that the color reaction of wood with strong acids was due to a lignin-carbohydrate complex and that its disappearance during sulfite cooking was caused by a cleavage of this complex.

According to I. H. Isenberg and M. A. Buchanan (66) some wood species give a purple-red color reaction on treatment with hydrogen chloride in methanol solution. Nothing was known about the mechanism of this reaction until recently it was shown (E. Adler, unpublished) that it is due to the presence of tannins of the catechin type, which are polyphenols. The coloring is then easily explained as a reaction between these polyphenols and the coniferaldehyde groups of lignin, catalyzed by the methanolic acid. The reaction is quite analogous to the normal phloroglucinol color reaction of wood, with the difference that the phenolic component (catechin tannin) is already present in the wood. J. C. Pew (66 a) has arrived at the same conclusion.

Another color reaction for the lignified parts of wood has been described

by R. Combes (66 b). Wood is treated for 12-14 hours with cold lead acetate solution or heated on the water bath for 30 minutes with lead acetate solution or a suspension of zinc oxide in water, washed, and treated for 5-15 minutes with hydrogen sulfide in water. After these operations the wood gives, on addition of concentrated sulfuric acid, a strong red-violet color. Combes believed, that some specific substance, possibly identical with Czapek's hadromal, is liberated by the primary treatment with lead acetate or zinc oxide and that H_2S then reduces this substance. The reduction product formed should then give a red color with sulfuric acid.

E. Adler and L. Ellmer (unpublished) have studied the nature of this color reaction. They found, that the pretreatment of wood with lead acetate or zinc oxide is superfluous. The red color is likewise obtained, when a sample of wood meal is mixed with a little sodium sulfide, and a few drops of concentrated or, still better, 75 % sulfuric acid are added. Another modification is treatment of wood meal, suspended in 50 % sulfuric acid, with hydrogen sulfide, washing, drying in a desiccator, and addition of concentrated or 75 % sulfuric acid. The mechanism of the reaction is, therefore, the following:

Some specific substance or group, present in the wood, reacts with H_2S in the presence of acids, and the reaction product formed gives a red color with strong sulfuric acid. Combes' view, that a liberation of the color-forming substance is brought about by lead acetate or zinc oxide treatment, is erroneous. The actual effect of the pretreatment of wood with these substances is, that upon the consequent treatment with H_2S , lead or zinc sulfide is deposited on the wood and that these sulfides then are decomposed by the sulfuric acid, giving H_2S , which, in presence of the strong acid, causes the color reaction.

The chemical nature of the substance responsible for this color reaction, has also been investigated. It has been found, that wood which has been subjected to a pretreatment with hydroxylamine, no longer gives the H_2S - H_2SO_4 -reaction. Furthermore, it has been shown, that coniferaldehyde gives the same color reaction as wood, when treated with H_2S and sulfuric acid of high concentration. Coniferaldehyde, dissolved in 50 % sulfuric acid, yields a precipitate on treatment with hydrogen sulfide. The precipitate no longer gives any phloroglucinol reaction, but does give the red color reaction with strong sulfuric acid.

It appears to be possible that the treatment with H_2S brings about a reduction of coniferaldehyde to coniferyl alcohol groups. (If free coniferaldehyde is treated with H_2S and 50 % H_2SO_4 , the coniferyl alcohol formed will readily polymerize under the influence of the acid). As a matter of fact, coniferin, the glucoside of coniferyl alcohol, as well as the free alcohol

give color reactions very similar to those obtained in Combes' reaction on treatment with conc. hydrochloric acid (24) or strong sulfuric acid.

Thus, five types of color reactions of wood, that is, the reactions with phloroglucinol or other phenols, the reactions with aromatic amines, the reaction with concentrated hydrochloric acid, the reaction of certain wood species with methanolic hydrochloric acid, and the reaction with hydrogen sulfide and strong sulfuric acid, can be ascribed to the coniferaldehyde groups present in the lignin.

Much has also been written about Mäule's reaction (67). C. Mäule found that a strong red color often appears when wood is treated successively with neutral potassium permanganate solution, dilute hydrochloric acid, and ammonia. E. Ungar (34, 68) checked this reaction, and found that the color sometimes fails to appear, especially in the case of spruce and pine (69). E. C. Crocker (70), who also studied Mäule's reaction, emphasize the fact that the interaction of wood and permanganate results in the formation of manganese dioxide, which reacts with the hydrochloric acid to give chlorine. The chlorine yields a chlorinated lignin, which gives a red color with ammonia or with other alkalis. It was found that hardwoods gave the characteristic red color, while softwoods yielded a pale brown color, which was not well defined (71).

W. G. Campbell and J. C. McGowan (72) report that the chlorine-sodium sulfite reaction of hardwoods seems to be identical with the "gallotannin reaction" described by C. A. Mitchell (73).

Among the many inorganic reagents for wood, we may also mention cobaltous thiocyanate, which gives a blue color in aqueous solution (74); vanadium pentoxide in phosphoric acid, which gives a yellow-brown color (75); zinc chloride solution, which gives a yellow color with substances containing lignin (76). These reactions are all quite unspecific, for in all cases where oxidation is involved, wood is not the only substance which gives the color reaction (44).

A new staining method for the microscopic examination of woody tissues has recently been described by G. Jayme and M. Harders-Steinhäuser (77). It is based on the observation that on treatment of wood with nitrogen tetroxide a yellow color develops in the lignified parts of the cell. This color turns to brownish-yellow, when alkali or organic bases, like triethanolamine, are added. In this way the small amounts of lignin present in the secondary wall of hardwood cells could be made visible.

B. PROPERTIES OF NATIVE LIGNIN

1. Lignin, Extractable with Organic Solvents. The primary aims of lignin research are to determine the constitution and properties of lignin,

and to learn in what form it occurs in woody tissue. To these ends it would be most desirable to separate the lignin from the other components of the wood without altering its chemical structure. This would be possible, if the lignin could, for example, be dissolved in neutral organic solvents.

P. Klason (78) believed that a substance which he obtained by extraction of spruce wood with hot alcohol was lignin. K. Freudenberg (79) also found that the extract obtained with hot mixtures of alcohol and benzene contained low-molecular-weight lignin, along with resin. The yield was insignificant, however. If the alcohol extraction was carried out at higher temperatures, dark-colored tars were obtained (80).

It is important to carry out the extractions at low temperatures, because of the strong tendency toward self-condensation shown by native lignin. F. E. Brauns (61) actually succeeded in extracting a substance, which he designated as "native lignin," by treating black spruce wood with alcohol at room temperature. It will be interesting to record the characteristics of this product.

The content of methoxyl was 14.8 %, which is exactly the value which E. Hägglund and O. Sandelin (81) had established indirectly for the native lignin of spruce. The latter authors found that the carbohydrate of spruce contained methoxyl equal to 0.56 % of the weight of the wood. When this is subtracted from the total methoxyl content of the wood (4.6 %) one obtains 4.04 % of the wood for the methoxyl of the lignin, and since the lignin constitutes 27.2 % of the wood, the methoxyl content of the lignin can be calculated to be 14.8 %. Brauns also found that his lignin showed the Wiesner reaction (red coloration on treatment with phloroglucinol and hydrochloric acid). It also reacted with phenol and hydrochloric acid to give a phenol lignin with a methoxyl content of 11.5 %, which agrees with that of preparations which H. Hibbert and his co-workers (82) had obtained from hydrochloric acid lignin and from Freudenberg lignin. The lignin also reacted almost quantitatively with thioglycolic acid, forming a product containing 10.5 % of methoxyl. This composition corresponds to the tetrathioglycolic acid lignin of B. Holmberg (83).

The lignin preparation of Brauns gives with concentrated hydrochloric acid the same emerald-green color which is observed when wood is treated with the same reagent (cf. p. 191).

The solution in methanol was yellow-brown in color: the addition of methanolic hydrochloric acid caused an almost instantaneous transformation to wine-red. When the HCl content of the methanol solution was 2 %, and the solution was refluxed for several hours, 35 % of the

lignin precipitated from the solution in the form of a condensation product, which was insoluble in dioxane and contained 20.85% methoxyl. The methoxyl content of the lignin remaining in the solution was 21.5%, which is exactly the same as that of the methanol lignin which is obtained by direct treatment of the wood under the same conditions (84). The formation of condensation products is directly dependent on the acid content of the alcohol; 0.5% of hydrochloric acid in the methanol does not cause any precipitation of the lignin.

The fact that part of the native lignin is precipitated from a boiling 2% solution of hydrochloric acid in alcohol supports the notion that the reason why relatively little of the lignin is dissolved out of wood by hot, acidified alcohol (cf. p. 237) is that a portion of the lignin undergoes condensation in the solid phase, and finally becomes insoluble (85).

F. E. Brauns agrees with B. Holmberg (84) and E. Hågglund (84) that the alcohol lignins are acetals, and even believes that he has demonstrated that two alcoxyl groups are bound as acetals to one molecule of lignin based on a molecular weight of approximately 840, corresponding to four original OCH_3 groups. The presence of a carbonyl group was also indicated by the formation of a phenylhydrazone. The lignin preparation contained two hydroxyl groups which can be methylated with diazomethane; one was phenolic, and the other, enolic.

The "native lignin" could be completely dissolved in hot sulfite solution, but sulfite had no dissolving action after the preparation had been methylated with diazomethane.

An alcohol-soluble lignin fraction, quite similar to that obtained from black spruce, was more recently prepared by F. E. Brauns (86) from Western Hemlock. Its ultraviolet absorption spectrum showed a maximum at 283 $\text{m}\mu$.

It should be pointed out that in both cases the yield of "native lignin" amounted to only 2-3 % of the total lignin.

A "native hardwood lignin" has been isolated from aspenwood by M. A. Buchanan, F. E. Brauns and R. L. Leaf, jr. (86 a). The purified product, which was obtained in a yield of 0.7% of the original wood, contained 19.5% methoxyl. The preparation contained one hydroxyl group per methoxyl group and one phenolic group per six methoxyl groups.

It is certainly true that the properties of Brauns' lignin agree in many respects with the results which have been obtained on lignin firmly bound in the wood (native lignin). These results will be discussed below.

The experiments of A. Guillemonat and P. Traynard (88) may also be mentioned in this connection. They used alcohol-benzene mixtures to

extract products from spruce which yielded a native lignin on reprecipitation from dioxane with ether. This lignin gave the color reaction with phloroglucinol. The addition of thiocyanogen made the presence of double bonds appear probable.

W. H. Steeves and H. Hibbert (87) acetylated oak wood which had been previously extracted at room temperature with 5% sodium hydroxide. The acetylated wood was extracted with chloroform, and the dissolved material treated with acetone. The acetone extract did not consist entirely of acetylated lignin, but a pure product could be obtained by further treatment with alkali and reprecipitation. When the acetyl residues had been split off, the product was found to be soluble in bisulfite at 110° C.

2. Firmly-Bound Native Lignin. The amount of lignin which is extractable with neutral organic solvents is very small, as has been mentioned above, amounting to only a few per cent of the total lignin.

By far the larger part of the lignin of wood is firmly bound to the woody substance, and can not be brought into solution with neutral organic solvents. The extraction of lignin by the methods to be described below causes more or less extensive changes to occur in the native lignin, due in part to condensation reactions. In order to determine the chemical properties of the bound native lignin, it would be necessary to liberate it by reactions which do not cause such changes.

Recently, W. Stumpf and K. Freudenberg (88a) reported that it is possible to extract the bulk of the lignin from wood meal (spruce and beech) by swelling the wood with water, replacing the water by dioxane containing 10-20 % of water, and extracting at room temperature with dioxane containing 1 % water and 0.35 % hydrogen chloride. The authors assume that the acid resolves hydrogen bonds between the lignin molecules or between lignin and polysaccharide molecules. On the basis of these experiments, Stumpf and Freudenberg believe that at least a large part of the lignin in the wood exists in a state similar to the alcohol-soluble "native lignin" of F. E. Brauns, i.e., in a comparatively low-molecular state (molecular weight about 1,000). The elementary composition of the spruce lignin obtained by Stumpf and Freudenberg was $C_9H_{8.7}O_{2.6}(OCH_3)_{0.98}$.

3. Reactions of Native Lignin with Sulfite. The solution of lignin with acid sulfites takes place in two steps, the first of which involves the sulfonation of the native lignin to a *solid lignosulfonic acid*. (This matter will be discussed in more detail in Chapter V.)

E. Hägglund, T. Johnson, and H. Busch (89) have investigated the speed of the sulfonation of native lignin.

Spruce sawdust from which the resin had been removed was heated with sodium sulfite solutions of various acidities. It turned out that the lignin took up sulfur more rapidly, the higher the hydrogen ion concentration. This may be seen from the following figures:

pH of the Sulfite Solution	Residue, in % of the Original Material	% S in the Lignin of the Residue
3.8	89.9	3.29
5.8	92.5	2.76
7.0	92.5	2.57

The sulfonation does not cease in alkaline sulfite solutions. Even at a pH of about 12, the residue was found to contain firmly bound sulfur. It is clear, however, that the speed of the sulfonation is very much decreased under these conditions.

When bisulfite was added to the double bonds of unsaturated aliphatic and aromatic carboxylic acids, it was found that the speed of sulfonation was directly proportional to the bisulfite ion concentration of the solution (90). If the sulfonation of the lignin involved this sort of a reaction, it would be expected that the uptake of sulfur would cease in alkaline solutions.

Further investigations have revealed that the sulfonation of lignin in the solid phase with neutral or faintly acid solutions (pH about 5) can not be made to go farther than to a compound containing 1 sulfur atom to 30-40 carbon atoms, even when the cooking is very much prolonged (89) (cf. also p. 206 and Ch. V, p. 119). This reaction has recently been studied more carefully by E. Hägglund, H. Erdtman, G. Aulin-Erdtman, and B. Lindgren (91, 92). Spruce sawdust from which the resins had been removed was heated for several days at 108°C with a sodium sulfite solution of pH 6. The sulfur uptake proceeded rapidly for the first hours, and then stopped completely. After several days the sulfur content corresponded approximately to a sulfonic acid with 1 sulfur atom to 1 lignin molecule of 40 carbon atoms.

Such "solid lignosulfonic acids," with low sulfur content, can be extracted from the wood according to the procedure described by C. Kullgren (93) for the extraction of lignosulfonic acid from sulfite pulps. In analogy to this procedure, the metal ions of the solid lignosulfonate are replaced by hydrogen ions by treating the sulfonated wood with cold dilute hydrochloric acid. The wood is then washed with water and finally heated with water at 80-90°C (91).

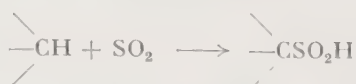
When aspen was used instead of spruce (94) it was found that the solution of the low-sulfonated lignin after cation exchange was very difficult. These lignosulfonic acids, with 1S to 50C, polymerized and precipitated out even in neutral solution when they were heated in water to 50-60 °C. The precipitate could be dissolved in sulfite cooking liquor, and the sulfur content then rose to 1S : 1.5 OCH₃. The resulting lignosulfonic acid could not be precipitated with organic bases; this may be due to an increase in the number of hydrophilic sulfonic acid groups or to a depolymerization. The above-mentioned lignosulfonic acids which had precipitated from neutral solution were poor in sulfur, and contained carbohydrate, most of which was pentosan. This fact constitutes strong support for the idea that the lignin of wood is chemically combined with the carbohydrates.

It was also found that the barium salt of the low-sulfonated lignosulfonic acid from spruce rapidly became insoluble when it was heated to 105-110 °C; this was presumably due to auto-condensation. This sensitivity toward heat is not shown by the normal lignosulfonic acids, containing 1S to 20C; the latter can be easily dissolved out at elevated temperatures with relatively acid buffer solutions which contain no sulfite. No polymerization or condensation then occurs. The sensitive groups are doubtless removed when the extra sulfite is taken up.

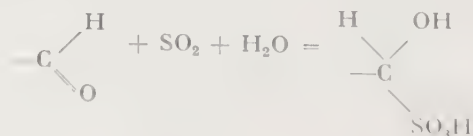
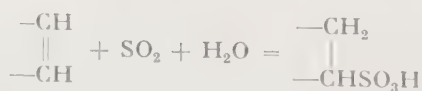
The question as to how the sulfurous acid is bound to the lignin may be discussed here.

P. Klason (95) discussed various possibilities at an early date.

The combination:

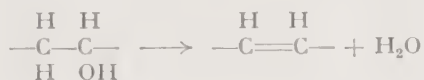


would lead to the formation of a sulfinic acid. However, since reduction with zinc and acid gives no mercaptans, and treatment with chloroacetic acid gives rise to no hydrogen chloride, it must be concluded that such acids are not present. (These reactions are characteristic of sulfinic acids.) According to Klason the following sorts of combinations then remained:



K. Freudenberg and his co-workers (96) treated isolated lignin with bromine in hydrobromic acid, and found that the lignin took up one atom of bromine for every methoxyl group. Somewhat more than the equivalent quantity of hydrogen bromide was formed at the same time. This indicated that bromine substitution was occurring. Only small amounts of acetyl groups were taken up when the lignin was treated with lead tetraacetate (97). Freudenberg concludes from these results that only unimportant numbers of aliphatic double bonds are present in the lignin molecule (cf. p. 289). The lignosulfonic acid can not arise, therefore, to any great extent, by direct addition of the sulfite to such double bonds.

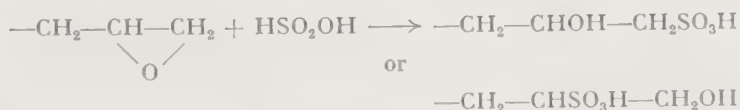
Freudenberg considered the possibility that water was first split off from an alcoholic group, giving rise to a double bond:



According to this scheme, the sulfonation would be accompanied by a decrease in the hydroxyl content.

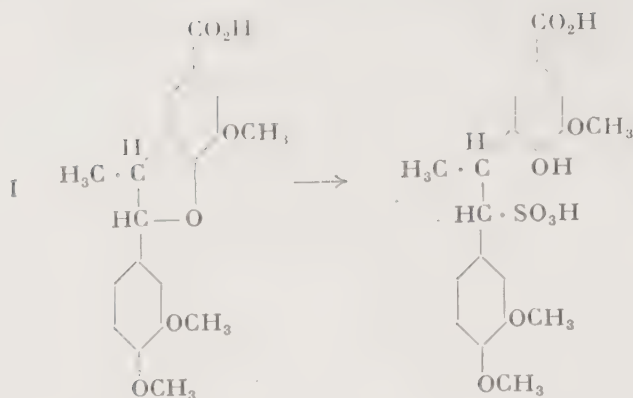
A viewpoint expressed by W. Fuchs, B. Elsner, and W. Stix (98), on the basis of the work of H. Bucherer (99), is hardly important any more. According to these workers, the sulfonation of lignin was supposed to take place in an aromatic nucleus; the reaction between bisulfite and resorcinol (or other dihydroxybenzenes) was considered to be the prototype of this reaction.

P. Klason (100) early proposed the possibility that the sulfite might be added to an ethylene oxide ring in the lignin molecule:

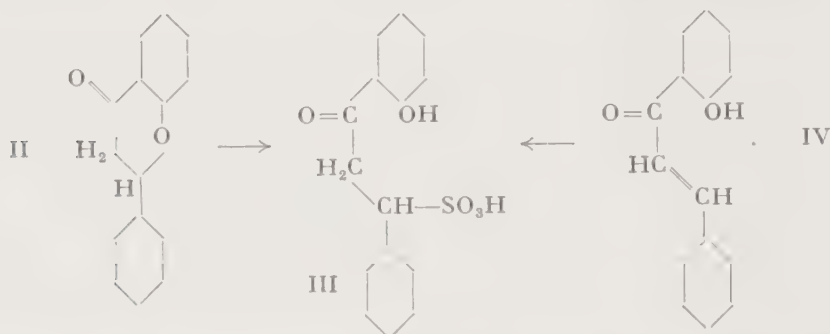


The possibility of the sulfonation of lignin through the opening of an oxygen ring was also considered later (101). K. Freudenberg (102) originally thought of a two-stage process. The first stage consisted in the opening of an oxygen-containing ring, with formation of one phenolic and one secondary hydroxyl group, the latter being then partly replaced by SO_3H , either directly, or after the splitting off of water.

As an example of a sulfonation involving the opening of a ring, K. Freudenberg and his co-workers (103) have cited the sulfonation of an oxidation product (I) of methylated dehydrodiisoeugenol, described by H. Erdtman (104):



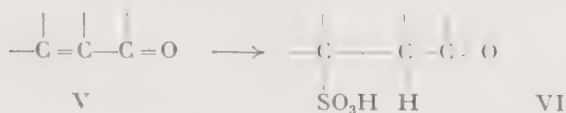
Some years later, H. Richtzenhain (105) showed that the oxygen ring in flavanone (II) is also opened and a sulfonic acid (III) is formed when the substance is heated with bisulfite or sulfurous acid solutions:



According to these two last-mentioned model reactions, the entrance of a sulfonic acid or thioglycolic acid group into the lignin molecule should result in a simultaneous formation of a free phenolic group. This seems, however, not to be the case (106 a-d). Furthermore, the oxygen ring cleavage is not at all a general reaction. Richtzenhain's experiments (105) show, that coumaran, coumaranone and flavan rings generally do not react with bisulfite. The splitting reactions mentioned above may be due to special activating influences exerted by the *p*-carboxyl group in the coumaran system (I) and by the carbonyl group in the flavanone (II).

Closely related to the flavanone studied by Richtzenhain is the chalcone (IV), which according to K. Kratzl and H. Däubner (107) easily reacts with bisulfite, giving the same sulfonic acid (III) as the flavanone (II). Systems like the flavanone II and the chalcone I have been supposed to be present in lignin by A. Russell (108) and by D. M. Ritter, D. E. Pennington, E. D. Olleman, K. A. Wright and T. F. Evans (109) (cf., however, p. 318).

Sulfonation experiments, carried out with numerous model substances, led Kratzl and co-workers (109 a, b) to the conclusion, that substances containing the conjugated system (V) are easily sulfonated (cf. also Klason, p. 219).



Since neither carbonyl groups nor ethylene linkages occur in lignin in appreciable amounts, Kratzl assumes that these conjugated systems are in some way "masked" in the lignin and are intermediately liberated during the sulfite cook. Examples of "masked" systems of this type might be the flavanones mentioned above, or acetals of aldol groups.

It must, however, be emphasized, that the sulfonated side-chains of lignosulfonic acid cannot have the structure shown in VI. It is a well-known fact, that the sulfo group in such 3-oxo-sulfonic acids is easily split off by treatment with alkali at room temperature, the α,β -unsaturated carbonyl compound being regenerated. Sulfite is split off instantaneously from cinnamaldehyde or coniferaldehyde hydrosulfonic acids (109 c, d), and even the bisulfite addition products of the chalcones (III) are decomposed, although at a somewhat lower rate, upon treatment with cold dilute alkali (109 e).

This discussion would not be complete without mention of a hypothesis offered by P. Klason (110), but not supported by any data. This hypothesis was based on the assumption that the so-called α -lignin is built up of guaiacylpropionaldehyde residues. In the native lignin these residues were supposed to be condensed with one another in the form of hemiacetals:



Free aldehyde groups were supposed to be formed first during the sulfite cooking; these groups would react with the bisulfite. Water would then split out, and the bisulfite would be firmly bound to the double bonds thus formed.

G. Aulin-Erdtman, A. Björkman, H. Erdtman and S. E. Hägglund (111) recently studied the reaction between certain cyclic acetals and bisulfite. They found that the cyclic hemiacetal (VII) reacted rather easily with bisulfite cooking liquor to form the sulfonic acid (VIII).



The possibility of sulfonation of carbinol groups according to the scheme:



has, for the first time, been discussed by B. Holmberg (112), on the basis of the similarity of the reactions of sulfite and thioglycolic acid

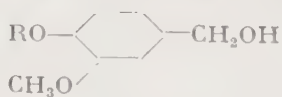


and of the investigations of A. Baeyer and V. Villiger (113), who found that sodium triphenylmethanesulfonate was formed by the reaction of triphenylcarbinol and sodium bisulfite.

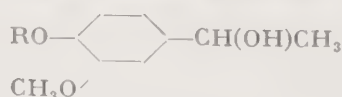
The assumption was supported by the fact that α -phenethyl alcohol (but not β -phenethyl alcohol) and diphenylcarbinol give the corresponding sulfonic acids, $\text{C}_6\text{H}_5\text{CH}(\text{SO}_3\text{Na})\text{CH}_3$ and $(\text{C}_6\text{H}_5)_2\text{CH}(\text{SO}_3\text{Na})$ on heating to 130°C with sodium bisulfite solutions, and that α -phenethyl alcohol showed the same behavior as did lignin also toward thioglycolic acid and ethyl alcohol (114).

K. Kratzl and H. Däubner (107) confirmed B. Holmberg's results by showing that phenylethylcarbinol, on sulfite cooking gives a phenylpropanesulfonic acid. Oddly enough, they found that ketols like α -hydroxypropioguaiacone [Hibbert (115)], methyl-benzoyl-carbinol, acetylbenzyl-carbinol, and benzoin do not react with bisulfite.

In B. Holmberg's model experiments with α -phenethyl alcohol the rate of sulfonation and the yield of sulfonic acid were rather low. Since it would be expected that substituents in the benzene nucleus would be of great importance for the reactivity, B. O. Lindgren (116) recently investigated the sulfonation of the following benzyl alcohols:



IX a: R = H
IX b: R = CH₃

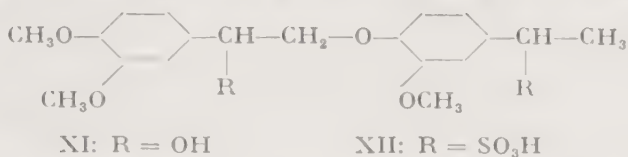


X a: R = H
X b: R = CH₃

He found that all these substances reacted rapidly and quantitatively when heated with bisulfite cooking acid, forming the corresponding benzyl sulfonic acids. These experiments strongly support B. Holmberg's view that in lignin hydroxyl groups in the α -position to the guaiacyl or syringyl nucleus are present and that they are, at least partly, the seat of the sulfonation reaction.

Lindgren further showed that his model substances readily condense with phenols added to the sulfite cooking acid, thus preventing proper sulfonation. This is in complete accordance with the observations concerning the competition of phenols and bisulfite in the sulfite cooking of wood (cf. p. 206 and chapter V, p. 446).

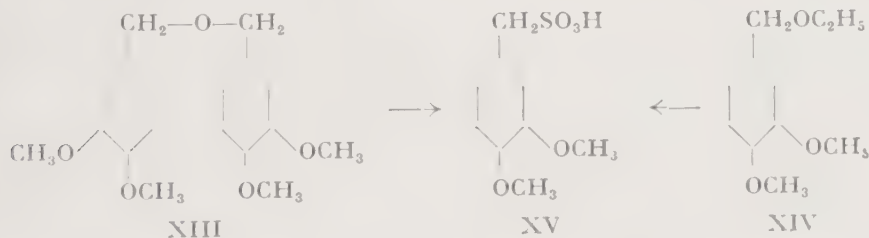
The conversion of a more complicated model of the benzyl alcohol type (XI) into the corresponding sulfonic acid (XII) by heating with sulfite cooking acid has been reported by H. Erdtman and B. Leopold (117):



B. Holmberg (114) has found that not only α -phenethyl alcohol, but also its ethyl ether reacts with thioglycolic acid, yielding α -phenethyl thioglycolic acid. Since the alcohol reacts not only with thioglycolic acid but also with bisulfite, one would expect that the ethyl ether would also react with bisulfite.

H. Richtzenhain (105) later extended these investigations to several aryl benzyl ethers, including guaiacyl ethers of phenylcarbinols, which were supposed to resemble lignin more closely in their chemical constitution. It was sometimes found that only bisulfite and sulfurous acid reacted, but not thioglycolic acid. This was also the case with *p*-nitrobenzyl and anisyl guaiacyl ethers.

Similar to the benzyl alcohols, benzyl alkyl ethers are easily sulfonated if they are activated by hydroxyl or alkoxy groups in the benzene nucleus. Thus, B. O. Lindgren (117 a) found that diveratryl ether (XIII) and veratryl ethyl ether (XIV) are readily transformed to 3,4-dimethoxytoluene-*o*-sulfonic acid (XV)



when heated with sulfite solutions of pH 1.4-3.7. Contrary to veratryl alcohol, diveratryl ether did not react with sulfite at higher pH values (about 6).

K. Freudenberg, W. Lautsch, and G. Piazzolo (118) have analyzed the liginosulfonic acids which they obtained at 70°C by stepwise sulfite cooking

of spruce wood with sodium bisulfite solutions rich in sulfurous acid. The main part contained 1S to 2CH₃O groups. The acids obtained after 4-days' cooking, which amounted to about 20% of the total, contained approximately twice as much sulfur, i.e., 1S per CH₃O. There were indications that small amounts of the acid—perhaps 1%—contained as much as 1½S per CH₃O.

One can not conclude, however, that a different kind of lignin is present in the residues after approximately three-fourths of it has been dissolved out. The real reason why the lignin finally becomes so difficult to dissolve is surely that the lignosulfonic acid or the lignin itself have stood for so long a time in contact with the hot sulfite liquor. This would make condensation unavoidable. The truth of this explanation is attested by the fact that the molecular weight of the dissolved lignosulfonic acids increases greatly from one fraction to the next. The lignosulfonic acids formed in this way obviously must be more extensively sulfonated than the normal ones before they can be dissolved.

The same conclusions may be drawn from investigations of W. Lautsch and G. Piazzolo (106 b), who examined two sulfite waste liquors from spruce pulplings. One was a technical rayon pulp liquor and the other was a laboratory liquor, from a moderately strong pulp. The progressive addition of 3,4-benzacridine hydrochloride yielded nine different fractions of precipitate, each of which was analyzed. By far the largest portion of the lignosulfonic acid contained 1S for every 20C, corresponding to 1S : 2CH₃O. Only a few per cent of the lignin contained twice as much sulfur.

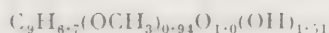
Elementary analysis and determination of functional groups showed further that the fractions with higher sulfur contents were lower in hydroxyl. The total hydroxyl was determined potentiometrically, by the Verley-Bölsing procedure, on samples of free lignosulfonic acid which had been dried at 55°C. Phenolic hydroxyl was determined according to K. Freudenberg and H. Walch (119). It was found that phenolic OH did *not* increase with increasing sulfonation. The sulfonation, at least at 70°C, would, therefore, not be accomplished by the opening up of benzofurane rings (103). In Freudenberg's opinion it is more likely that ether linkages not attached to phenol groups are involved, possibly benzyl alkyl ether linkages of the type occurring in pinoresinol (cf. p. 341).

As a matter of fact, B. O. Lindgren (117 a) has recently shown that pinoresinol yields a sulfonic acid on heating with sulfite solutions at pH 4-6. At lower pH, i. e., with normal sulfite cooking acid, pinoresinol is converted into a resinous product with low sulfur content [H. Erdtman (120)].

The further sulfonation of low-sulfonated lignosulfonic acids [E. Hägglund and co-workers (89, 91, 92) cf. page 197] appears to be a very promising line of research concerning the sulfonation mechanism. The starting material is prepared by cooking disintegrated spruce wood with a sodium bisulfite-sulfite solution of pH 5 for 14 hours at 135°C (89), replacing the sodium ions of the sulfonated wood by hydrogen ions, and extracting the free lignosulfonic acid with water at 80–90°C (91). By heating a lignosulfonic acid of this type with ordinary sulfite cooking acid for different periods of time, H. Erdtman, B. Lindgren, and T. Pettersson (121) obtained three additional lignosulfonic acids with increasing sulfur content. The hydroxyl group content of the four preparations was determined by a special acetylation procedure. In the following table, the data obtained on the composition of the starting material (A) and the further sulfonated preparations (B-D) are given:

Lignosulfonic acid	C	H	OCH ₃	—O—	—OH	—SO ₃ H
A.....	9	6.6	0.94	1.0	1.20	0.28
B.....	9	6.5	0.96	0.6	1.17	0.41
C.....	9	6.8	0.94	1.3	1.01	0.44
D.....	9	7.1	0.93	1.2	0.81	0.77

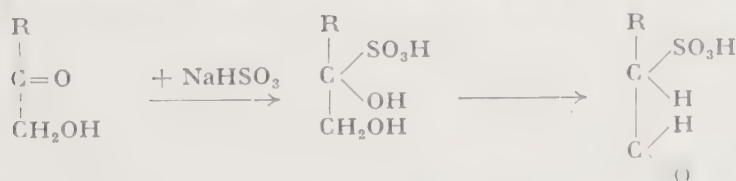
By substituting OH for SO₃H and calculating the average composition of the "lignin" corresponding to the acids A-D, the following formula has been obtained:



From the figures given in the table, it is obvious, that —OH-groups disappear when —SO₃H-groups are introduced into the molecule. It can also be seen, that for each sulfonic acid group introduced, one hydroxyl group has been removed.

Several possibilities may be advanced concerning the chemical nature of these hydroxyl groups and the reactions which make them disappear.

E. Hägglund and G. Menzinsky (121 a) found that aliphatic ketols, like glycolaldehyde and monohydroxyacetone, react with nearly neutral sulfite solutions forming stable sulfonic acids, probably according to the following mechanism which involves the loss of a hydroxyl group:



According to Kratzl and Däubner (107), however, aromatic ketols, such as α -hydroxypropioguaiacone, are not sulfonated when heated with

sulfite cooking acid. Therefore, the occurrence of reactions of this type in the sulfonation of lignin is still uncertain, and further experimental work is needed on this question.

From the model experiments of B. Holmberg (112, 114) and B. Lindgren (116), it is known that the hydroxyl groups of properly substituted benzyl alcohols are readily replaced by sulfonic acid groups, and it seems therefore probable that this type of reaction is involved in the further sulfonation of low-sulfonated lignosulfonic acid, carried out by Erdtman, Lindgren and Pettersson (121).

H. Erdtman and co-workers (111) have reported still another model sulfonation which involves the replacement of OH by SO_3H , i.e., the sulfonation of a cyclic hemi-acetal (cf. page 201).

There are several indications of the presence, in lignin, of at least two different types of groups undergoing sulfonation.

As already mentioned (cf. page 197, cf. also Ch. V, page 419), the rapid sulfonation of wood at pH-values near 7 ceases when a limiting value of 1S per 3-4 OCH_3 has been reached. The lignosulfonic acid formed remains in a solid state in the wood. Only at a lower pH, for instance, when normal bisulfite cooking acids are used, is the low-sulfonated lignosulfonic acid dissolved and further sulfonated.

In order to explain this second step of sulfonation, it has been assumed (112, 121 b) that the lignin molecules in the wood are linked by chemical bonds either with other lignin molecules or with carbohydrate constituents. The dissolution of the solid, low-sulfonated lignosulfonic acid which is formed during the first stages of a sulfite cook, should, then, consist of a hydrolytic cleavage of the linking groups followed by further sulfonation of these groups.

A similar explanation has been given to the above mentioned hot water extraction of lignosulfonic acid from sulfonated wood, in which the sodium ions have been replaced by hydrogen ions. In this case also, the dissolution is brought about by an hydrolysis. It is catalyzed by the hydrogen ions of the solid lignosulfonic acid. (cf. pages 216-218).

The existence of two groups with different reactivity has also been discussed on the basis of results obtained in the examination of the relationships occurring between the sulfonation and the phenolization of lignin. At the low pH prevailing in a normal bisulfite cooking acid, lignin is readily condensed with phenols. The addition of resorcinol and other polyphenolic compounds to a sulfite cook of spruce wood inhibits the dissolution of lignin as does the presence of the phenolic stilbene derivatives in the sulfite cook of pine heart wood (121 c, d, e, h; cf. also Chapter V, page 414). The phenol-lignin-condensation, however, is sup-

pressed if the sulfonation is carried out at a higher pH, for instance with NaHSO_3 or mixtures of NaHSO_3 and Na_2SO_3 . Under such conditions, phenolization does not take place, but instead the sulfonation of a "group A" occurs, yielding a solid, low-sulfonated lignosulfonic acid. Since the sensitive group A has been blocked by sulfonation, the sulfite cook can be accomplished with normal cooking acid, in spite of the presence of phenols. Therefore, it has been assumed that there is a "group B", which is converted into a sulfonic acid group only under acid conditions. H. Erdtman (121, 121 d, cf. 116) has characterized the properties of "group A" and "group B" as follows:

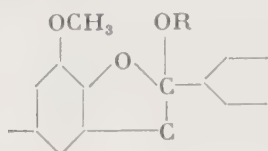
- Group A. 1) Is sulfonated easily with sulfite solutions at pH 1.5-2 and at pH > 3.5
- 2) Reacts more quickly with phenol than with bisulfite at pH 1.5-2
- 3) Reacts more quickly with bisulfite than with phenol at pH > 3.5
- Group B. 1) Is sulfonated easily with sulfite solutions at pH 1.5-2
- 2) Does not react at all or only slowly with sulfite solution at pH > 3.5
- 3) Reacts more quickly with bisulfite than with phenol at pH 1.5-2
- 4) Does not react at all or only slowly with phenol at pH > 3.5

From the experimental facts known at present, it appears as if hydroxyl groups in the benzyl alcohol position, such as in vanillyl and veratryl alcohol, behave like group A (121 f, 116).

Erdtman (121 g) assumes that group B might be identical to the group connecting lignin molecules with each other or with carbohydrates in the wood. Hägglund (121 b) has previously suggested that these groups may be of a carbonyl nature, and that the linkages, consequently, may be of an acetal character. The presence of acetal groups in lignin found support in the following observation of C. Kullgren (93): The calcium ions, of calcium lignosulfonate present in the solid state in strong pulp, were replaced by hydrogen ions, and the sulfonic acid brought into solution by heating with alcohols. Alkoxy groups were found to have been introduced into the resulting sulfonic acid. These groups were assumed to be present as acetal groups. The dissolution then might be explained as a re-acetalization of acetal groups present in the original lignin (93, 121 b).

Recently, H. Erdtman (121 g), has given this view a more precise formu-

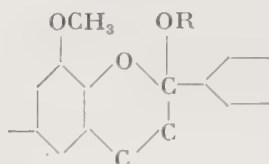
lation by suggesting that the carbonyl groups might occur in the form of cyclic acetals like I or II:



I a: R = H

I b: R = lignin or carbohydrate

I c: R = SO₃H



II a: R = H

II b: R = lignin or carbohydrate

II c: R = SO₃H

In wood, the residue R is assumed to consist of another lignin molecule or a carbohydrate molecule (I b, II b). This residue should be split off by acid hydrolysis. Thus, the dissolution of solid lignosulfonic acid from low-sulfonated wood, according to the procedure of C. Kullgren, should result in a hydrolysis of groups I b or II b so that the resulting, soluble lignosulfonic acid should contain groups I a or II a. Heating of the dissolved, low-sulfonated lignosulfonic acid with bisulfite solution should convert the liberated OH-groups of I a or II a into SO₃H-groups (I c, II c).

The non-cyclic acetal bond of I b or II b should also be split on heating with acid bisulfite solution, in which case the residue —OR should be replaced by —SO₃H.

As yet, only one model experiment has been described, which supports the convertability of such cyclic hemi-acetals into sulfonic acids (111. cf. p. 201).

The recent model experiments of B. O. Lindgren (cf. p. 203) showing that benzyl alkyl ethers and dibenzyl ethers are easily split and converted into benzyisulfonic acids on heating with acid sulfite solutions, suggest the alternative explanation that "group B" in lignin consists of benzyl ethers (117 a). It was found that the behavior of diveratryl ether toward sulfite and phenols corresponds to the characteristics given for "group B" under points 1, 2, and 4 (see p. 207). However, the characteristic given in point 3 is not fulfilled by diveratryl ether, its sulfonation being strongly inhibited by phenols at pH 2. This fact seems, however, not to contradict the benzyl ether theory of "group B". The characteristic of "group B" given under point 3 had been formulated by H. Erdtman on the basis of the following facts:

(a) lignin cannot be dissolved from wood in the presence of phenols when acid sulfite solutions are used,

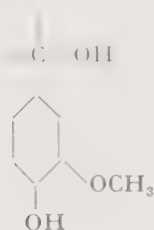
(b) a dissolution with acid sulfite solution can be achieved, if the wood has been pre-sulfonated with neutral or weakly acid sulfite solutions.

The fact that lignin products obtained according to (b) are soluble,

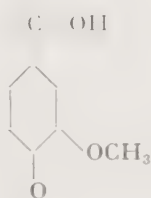
made H. Erdtman believe that no condensation of the low-sulfonated lignin with the phenols present had taken place. Lindgren (117 a) points out, however, that condensation products between low-sulfonated lignin and phenols can be water-soluble. As a matter of fact, it has been shown that water-soluble condensation products are formed, if isolated low-sulfonated lignin is heated with sulfite cooking acid in the presence of resorcinol [H. Erdtman (121 d)] or β -naphthol [B. O. Lindgren (117 a)].

In the light of these experiments the theory concerning the nature of the sulfite-reactive groups in lignin presents itself as follows:

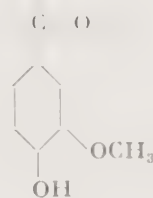
Lignin contains a type of groups ("group A"), consisting of hydroxy- or alkoxy-benzyl alcohol residues (I a, b) and possibly hydroxybenzyl alkyl ether residues (Ic):



Ia

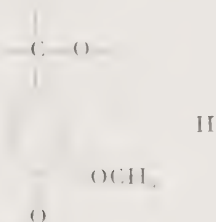


Ib



Ic

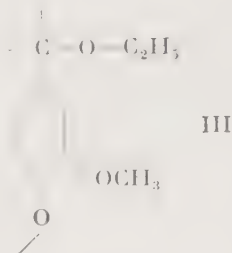
"Group B" will then be represented by the alkoxybenzyl alkyl ether type (II):



II

According to the model experiments described above these types of groups fulfill the requirements given for "group A" and "group B", respectively. On sulfonation of wood at neutral or weakly acid conditions, only the groups I a, b, and c will be sulfonated. The benzyl ether bond in group II is hydrolyzed only at more acid conditions; therefore, it is sulfonated only on cooking with acid sulfite solutions. It is also hydrolyzed to the corresponding alkoxybenzyl alcohol group (I b), when low-sulfonated liginosulfonic acid is extracted from wood with hot water according to the procedure of C. Kullgren (cf. p. 197). If this extraction is carried out with ethanol instead of water, an alcoholysis of the original

benzyl ether bond will take place, resulting in the formation of benzyl ethyl ether groups of type III:



This type of reaction — the re-etherification of benzyl ethers — has been shown to proceed very readily in model experiments (E. Adler and K. J. Björkqvist, cf. p. 288). On further heating with acid sulfite solutions the ethoxyl groups in the ethoxylated low-sulfonated lignosulfonic acids are replaced by sulfonic acid groups (121 i).

The presence of benzyl ether linkages between lignin molecules or between lignin and carbohydrate molecules has already been suggested by B. Holmberg (112, 114), who also assumed that they may react with sulfite. A comparison between the rate of lignin dissolution from spruce wood and the hydrolysis of diveratryl ether on heating with sulfite solutions of different pH has shown that the pH dependence of both processes is very similar [Lindgren (117 a)].

In the foregoing an attempt has been made to review the present concepts concerning the mechanism of lignin sulfonation and dissolution. It should be pointed out that there are still some facts which cannot be explained on the basis of the theories presented above. For instance, there is no explanation of the fact that lignin is not dissolved by a normal sulfite cooking procedure, if the wood has been methylated with diazomethane and dimethylsulfate prior to sulfite cooking. It is obvious that further experimental evidence is needed to clarify this problem.

In this connection the spectrophotometric results of G. Aulin-Erdtman (106 d, 111, 122) are of interest. They show that the further sulfonation of a low-sulfonated lignosulfonic acid with bisulfite cooking acids of normal composition has no appreciable effect upon the ultraviolet absorption (Fig. 49). This means that sulfonation of lignin, or at least of the low-sulfonated lignosulfonic acid, is certainly not accompanied either by elimination or formation of double bonds ($-\text{C}=\text{C}-$ or $\text{C}=\text{O}$) in conjugation with the aromatic rings. Furthermore, an opening of the oxygen ring in benzofuran systems seems very improbable (111, cf. however, E. Jones, 122 a).

The same conclusions have been drawn by P. W. Lange (123), who showed that the ultraviolet absorption of native lignin in the wood cell does not undergo appreciable changes when the wood is subjected to sulfite cooking.

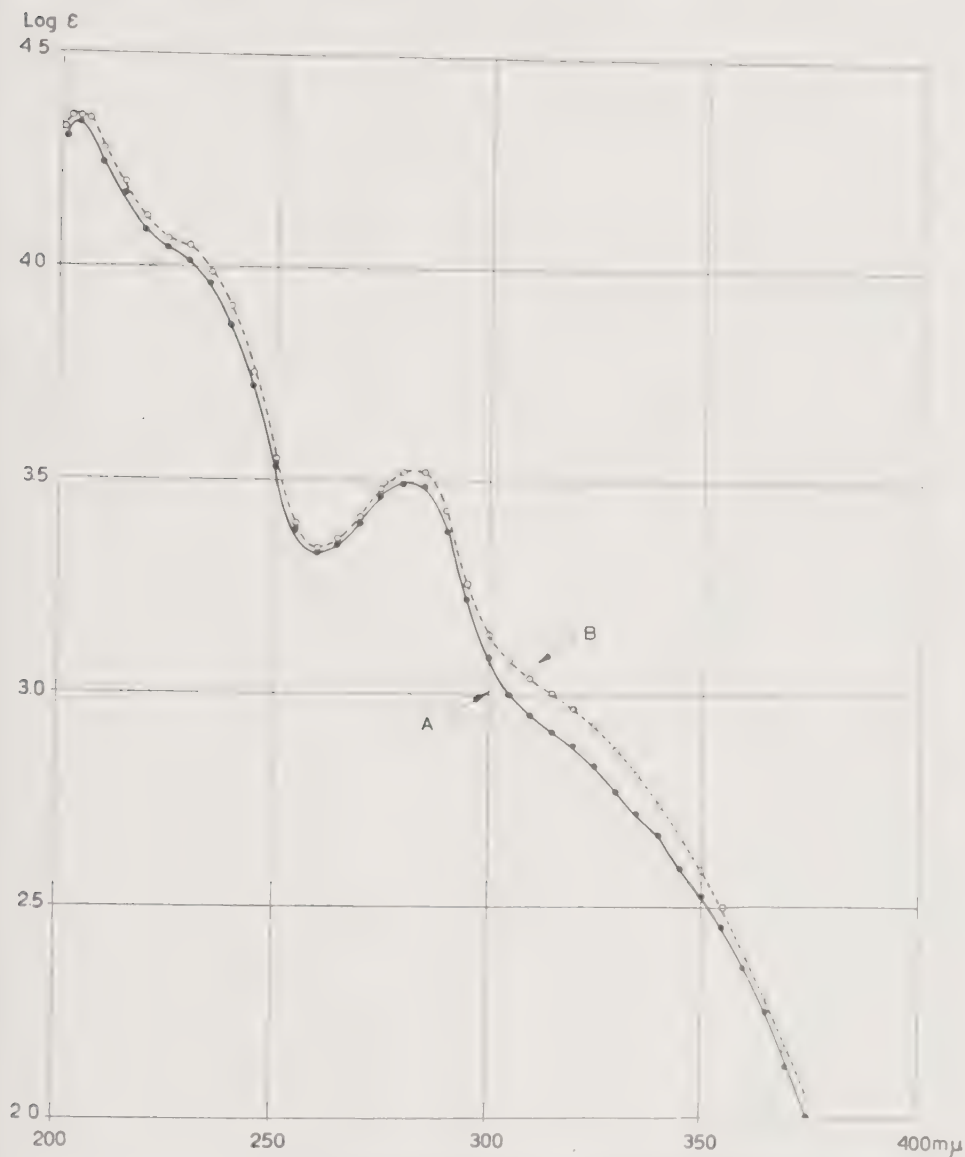


Fig. 49. Ultraviolet absorption of lignosulfonic acids.

A, low-sulfonated product, S:C=1:34. B, preparation A, further sulfonated, S:C=1:13.

Attempts to introduce further sulfo groups into lignosulfonic acids by heating them with sulfite cooking acid, showed that this was only possible with the lignosulfonic acids formed during cooks with sodium bisulfite solutions or with cooking liquors containing comparatively high percentage of lime. It was also of importance that the cooking not be

allowed to proceed too far. Lignosulfonic acids from the waste liquors from the preparation of rayon pulp were not further sulfonated to any appreciable extent. It is evident that under these conditions, where the acidity and temperature are considerably higher than in the cooking of hard sulfite pulps in well-buffered liquors, a change in the lignin molecule takes place which finally reduces its ability to react with sulfite (92).

Investigations by E. Hägglund and J. Holmberg (106 a) have shown that the methylation of wood with dimethyl sulfate or diazomethane makes delignification with sodium bisulfite more difficult. Alcoholic hydrochloric acid has a similar effect on wood. I. K. Buckland, F. E. Brauns, and H. Hibbert (123 a), as well as F. E. Brauns and D. S. Brown (123 b), have also shown that sprucewood meal, which has been treated with diazomethane until the lignin has a final methoxyl content of 21%, can no longer be delignified with bisulfite solution. Similarly, Brauns' "native lignin", which is dissolved when heated with bisulfite cooking acid, becomes insoluble after methylation with diazomethane. Freudenberg and co-workers (123 c) had previously stated that wood meal which had been methylated to a lignin methoxyl content of only 18 to 19% still can be delignified by a bisulfite cook. As yet, there is no satisfactory explanation of these phenomena. Acetylation of wood with acetic anhydride in pyridine does not seem to affect the sulfonation.

The properties of solid and dissolved lignosulfonic acids will be discussed later.

4. Reactions of Native Lignin with Hydrogen Sulfide and with Alkali Sulfides. Investigations of E. Hägglund (124) have shown that spruce wood reacts readily with hydrogen sulfide, and that the native lignin takes up sulfur during this process. Hydrogen sulfide is taken up from its water solution both pure and buffered. Most of the sulfided lignin (thiolignin) can be dissolved out of the wood with hot soda solutions as well as with pyridine, dioxane, or 75% ethanol.

If the sulfidation is carried out at pH 7 and 100° C during 72 hours, about 10% of the lignin can be dissolved by the above solvents. Eight alternate treatments of spruce wood with hydrogen sulfide and with solvents dissolved about 60% of the lignin. Grinding the wood in a colloid mill or pretreatment with reagents such as acids, alkalies, or chlorine does not substantially improve the yield of dissolved thiolignin, nor are better results obtained by the use of a large excess of hydrogen sulfide or with hydrogen sulfide dissolved in pyridine or 75% ethanol. The yield of thiolignin, however, increases when the reaction time is prolonged or the temperature elevated. Thus, when cooking spruce wood at 170° C with

hydrogen sulfide dissolved in pyridine solution, about 90% of the lignin is dissolved in 17 hours. The formation of thiolignin at 100°C increases with increasing pH until about 8.5 and remains thereafter fairly constant. Therefore, it appears to be probable that the main reagent is the hydrosulfide ion (SH^-) and not the undissociated hydrogen sulfide nor the hydroxyl ion (124 a).

The thiolignins thus obtained contain 7-17.5% sulfur in organic combination. They are weak acids, approximately of the strength of phenol, and show an equivalent weight of about 300. Their molecular weights are about 1,000. On treatment with methanol-hydrochloric acid they are not methoxylated. Boiling with sodium hydroxide solution at 100°C does not remove any sulfur, whereas raising the temperature to 160°C causes the removal of considerable amounts of sulfur, partly as sulfide. Wood is also sulfided on boiling with sodium hydrosulfide solutions and the thiolignin formed can be completely dissolved with sodium hydroxide at 100°C or partly dissolved by extraction with 75% ethanol. This thiolignin contains only 5-9% S, and its equivalent weight is about 200, which is the same value as is found for the sulfur-free alkali lignins. The sulfur seems to be bound in the organic sulfide form. If spruce wood is heated with NaSH solutions in the presence of NaOH at 160°C, the lignin is extracted and contains comparatively little sulfur (1%), even if high concentrations of NaSH have been used.

Hydrochloric acid lignin, cuproxam lignin, the "native lignin" of F. E. Brauns, and sulfur free alkali lignin also take up sulfur when heated with NaSH solutions (125, 126).

Even slight sulfidation of wood makes subsequent sulfite pulping nearly impossible, even though the lignin is sulfonated to an insoluble lignosulfonic acid. If, however, the sulfided wood is sulfonated first with sodium bisulfite at a relatively high pH (about 5.5), and then with an ordinary bisulfite cooking acid of lower pH, normal pulping takes place.

When lignosulfonic acids or methanol lignin are treated with hydrogen sulfide at pH 7 and 100°C, only small amounts of sulfur are taken up. It, therefore, seems possible that the same groups in the lignin which react with sulfite to give lignosulfonic acid or with methanol, in the presence of hydrogen chloride, to give methanol lignin, also react with hydrogen sulfide or sodium hydrosulfide to give thiolignin.

For further discussion of the reaction between lignin and sulfides see Chapter VI.

5. Reactions of Native Lignin with Alcohols, Mercaptans, and Phenols.

It has already been stated that there is a remarkable similarity between

the reactions of the native lignin with sulfite, and with alcohols, or mercaptans. In the latter case, too, the reagents are bound by the native lignin even in the solid phase. Part of the resulting compound is dissolved in the reagent during the course of the reaction, but the remainder must be extracted with alkali. Details of the preparation and properties of these compounds will be given later.

6. Reactions of Native Lignin with Halogens. P. Waentig and W. Gierisch (127) found that woods take up chlorine in definite quantities. From these "chlorine numbers" (cf. also p. 331), and the chlorine numbers of the lignin isolated according to Willstätter's method, it is possible to calculate the lignin content of the woods. Bromine has a similar action. The formation of chloro- and bromolignin occurs by substitution; a quantity of hydrogen halide equivalent to the halogen taken up by the lignin is evolved.

Iodine is also taken up by wood. According to H. Pauly and his co-workers (128) the iodine uptake occurs through chemical addition. No substitution or oxidation occurs with iodine.

7. Reactions of Native Lignin with Hydrogen Halides. Lignin takes up hydrogen chloride to form a loose addition compound (129). Coniferous wood takes up a quantity of hydrogen chloride equal to 8% of the lignin content, corresponding to HCl to an equivalent weight of 400 (130). This result can be reconciled with the assumption that one atom of ether oxygen is present in a section of the lignin molecule of the weight 400, probably in the form of a cyclic ether (131).

8. Oxidation of Native Lignin. Heating of spruce wood to 160 C in the presence of nitrobenzene and alkali resulted in yields of vanillin ranging up to 25% of the weight of the lignin. Lignin products, like cuproxam-lignin, Willstätter-lignin, and lignosulfonic acid, gave at most 20% of vanillin. Wood also yielded amounts of guaiacol and vanillic acid equal to about 1% of the lignin. Altogether about 40% of the lignin was recovered in the form of vanillin or similar products (132).

R. H. J. Creighton, R. D. Gibbs, and H. Hibbert (133) determined the yields of vanillin and other aromatic aldehydes obtained by oxidation of woody material with nitrobenzene in alkaline solution. It was found that ferns (*Pteridium*) gave only vanillin, in amounts equal to 30% of the lignin, as determined with sulfuric acid. *Cycas revoluta* also gave vanillin, in lower yields. All the conifers with few exceptions (genera *Podocarpus* and *Tetraclinis*) give only vanillin (19-24%) as does the ginkgo tree. The genera *Ephedra* and *Gnetum* behave like the angiosperms, which on

oxidation give both vanillin and syringaldehyde. Among the angiosperms the dicotyledons all show great similarities, with the possible exception of certain primitive families. The ratio of vanillin to syringaldehyde was usually 1:3 for the angiosperms; the total yield was high, running 30-50%. The monocotyledons were less fully investigated, but it was found that relatively less syringaldehyde was formed. In the case of certain grasses, like corn (maize) and rye, small amounts of *p*-hydroxybenzaldehyde were formed. This indicates the presence of a hitherto unknown structure element in the lignin. The wood which gave syringaldehyde also gave a positive Mäule's reaction, while a negative reaction was given by woods which gave no syringaldehyde.

W. Lautsch, E. Plankenhorn, and F. Klink (134) in Freudenberg's laboratory have also obtained 12-13% of vanillin by heating spruce sawdust with 10% potassium hydroxide in the presence of oxygen and cobaltic hydroxide.

It should be mentioned finally, that B. Holmberg (135) obtained 1.6 g. of an oxidation product containing bromine by the action of hypobromite on 10 g. of spruce sawdust. This product had many of the properties of a lactone. The elementary composition was 56.5% C, 4.9% H, 10.1% CH_3O (calculated on a bromine-free basis).

Holmberg later described this product in more detail (136). The composition was constant within narrow limits:



When the Br and CH_3 were replaced by H, the product had the composition: $\text{C}_9\text{H}_{8.45-8.7}\text{O}_{4.6-4.95}$. Holmberg believes that these oxidation products consist of carboxylic acids which have been partially converted to the corresponding lactones. The molecular weight agrees with that of lignothioglycolic acid. It is possible that the lignin products from bromine-alkali solutions arise by the opening of the ring in every other C_9 unit, with the formation of two carboxyl groups. The methoxyl content was doubled by methylation with dimethyl sulfate. Thioglycolic acid reacts with the brominated product to form products with low sulfur content, and also with the methylated bromination products; methoxyl is split off in the latter case. It is possible that a tertiary hydroxyl group, or a benzyl alcohol group is involved in these reactions.

C. LIGNIN PREPARATIONS

1. Lignosulfonic Acid

a. Dissolution of Lignosulfonic Acid. Two separate steps can be distinguished in the sulfite pulping process. These are (1) the sulfonation of

the lignin in the solid phase, and (2) solution of the lignosulfonic acid so formed. These processes will be discussed in more detail in Chapter V. Only the following matters, which seem to have a bearing on the properties of the lignosulfonic acid, will be mentioned here.

Fundamental to the attainment of a deeper insight into the processes involved in sulfite cooking was the establishment of the fact that a solid lignosulfonic acid was necessarily formed in the wood as a first step, and that this solid acid could then be dissolved, provided a certain hydrogen ion concentration was maintained (137). Shortly thereafter, it was found that the velocity with which the lignosulfonic acid was dissolved out by buffer solutions was directly proportional to the hydrogen ion concentration (138). And finally, it should be noted that these hydrogen ions can come from the solid lignosulfonic acid as well as from the surrounding fluid, depending on the conditions during the process of solution (139).

Solid lignosulfonic acid can be prepared by treating water solutions of lignosulfonic acid with strong mineral acids, like hydrochloric acid. It was found that although the resulting product was insoluble in water, it was extensively dissociated into ions (140). It is, therefore, to be considered as a strong acid, even in the solid form. [The solid lignosulfonic acid in sulfite pulp was later investigated by C. Kullgren (141), who used the same method and came to the same conclusions.] This acid behaves very much like a permutite; that is, it readily exchanges its cations for others. C. Kullgren and C. Du Rietz (142) studied this property in more detail. E. Öman (143) had already found that sulfite pulp rapidly exchanges its calcium for other metals; the investigations of E. Hägglund and his co-workers, mentioned above, demonstrated that the calcium of the solid lignosulfonic acid was here involved.

When the calcium is thus exchanged for hydrogen, giving a free lignosulfonic acid, and the pulp is then heated to moderately high temperatures in water or alcohol, the lignosulfonic acid goes into solution. This behavior was first observed by C. Kullgren (141, 144). These reactions have proved to be most useful in explaining the mechanism of the solution of the lignin (145), for if one assumes that the hydrogen ions accelerate the dissolving out of the lignosulfonic acid catalytically, the rate of solution of the free solid lignosulfonic acid must at all times be proportional to the "concentration" of the lignosulfonic acid and to the hydrogen ion concentration in the solid phase. This would mean that the reaction would be of the second order. The following experimental results may be quoted:

Time of Heating in hours	Lignin in Residue % of Original Lignin	$K_I = \frac{1}{t} \ln \frac{a}{a-x}$	$K_{II} = \frac{1}{t} \frac{x}{a(a-x)}$
0	100	—	—
$\frac{1}{2}$	88.1	0.25	0.42
$1\frac{1}{3}$	76.5	0.24	0.42
$2\frac{1}{2}$	60.5	0.20	0.42
$4\frac{1}{2}$	46.1	0.17	0.42
14	29.6	0.08	0.27

From these experiments it is clearly evident that the reaction proceeds bimolecularly until about 70% of the acid has gone into solution. The reaction then slows down; i.e., the rate constant decreases. This is probably due to the fact that a condensation ("reversion") of the liginosulfonic acid to larger units sets in, or else that residues of previously condensed lignin remain, which are more difficult to dissolve.

The fact that the reaction is accelerated by the addition of acid is in agreement with the theory. This acceleration may be seen from Fig. 50, which gives the curves for the rate of solution; it will be seen that the hydrogen ions of the surrounding solution have a strong catalytic effect. It is not true, therefore, that the free solid liginosulfonic acid alone causes

the dissolving process. *This process is due solely to the hydrogen ions inside the solid phase, whether they come from the liginosulfonic acid, itself, from the acid of the surrounding solution, or from both.*

The partition of the hydrogen chloride between the solid phase and the aqueous solution in the experiments of Fig. 50 can be calculated from the speed with which the lignin is dissolved out. The acceleration of the speed of solution by 1 N hydrochloric acid is about 80%. The acceleration would turn out to be approximately the same if the "concentration" of the liginosulfonic acid in the solid phase were 1 N, and the distribution were cal-

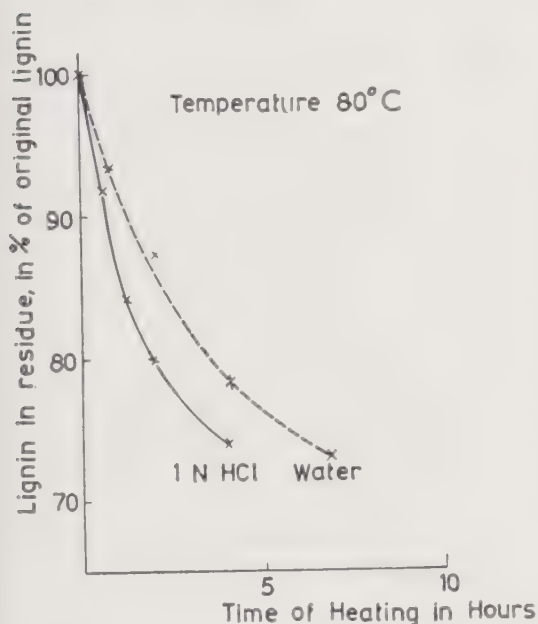


Fig. 50. Speed of dissolution of liginosulfonic acid from pulp by water or hydrochloric acid.

culated according to the Donnan equilibrium. The fact that 0.1 N hydrochloric acid causes practically no acceleration is in agreement with these facts, for a calculation shows that the acceleration to be

expected would be only 1%, and this could not be observed experimentally. These relationships are presented graphically in Fig. 51.

Fig. 51 also gives curves which show the velocity of solution with 0.1 *N* hydrochloric acid containing various amounts of sodium chloride. With 1 *N* NaCl the velocity dropped to approximately 20% of its original value, and with 0.1 *N* NaCl, it decreased to 60%. However, when the hydrogen concentration was brought to 1 *N*, in the presence of 0.1 *N* NaCl, the velocity of the reaction increased by 75%, in comparison to that with

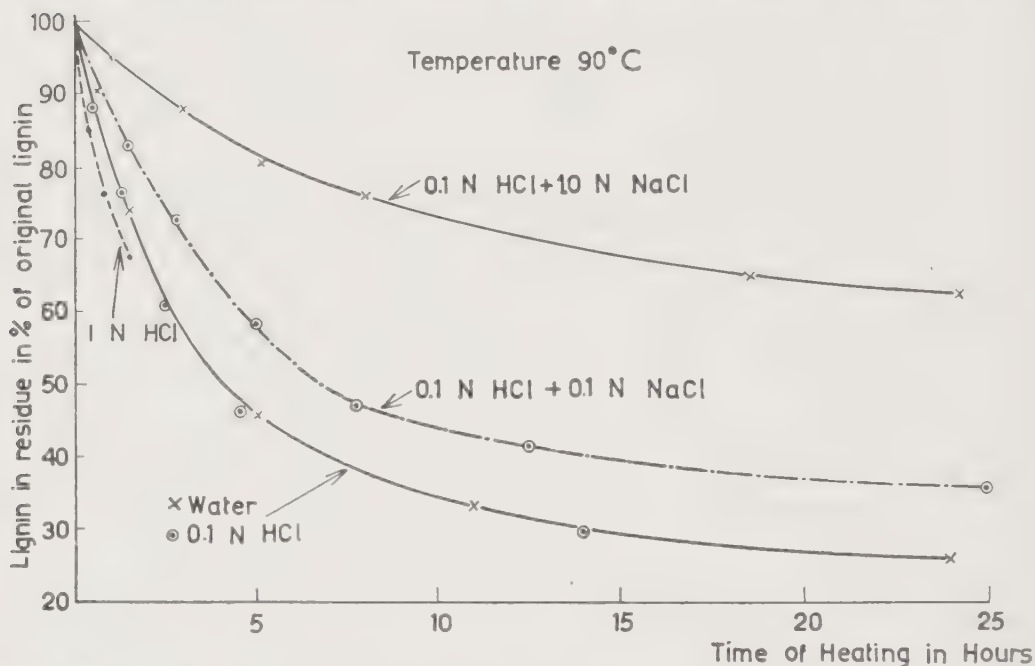


Fig. 51. Speed of dissolution of lignosulfonic acid from pulp by solutions of various compositions.

water alone; this result was to be expected on the basis of the theory (145, 146). F. E. Brauns and D. S. Brown (146) believe that a rearrangement occurs when solid lignosulfonic acid is changed to the soluble form. According to these authors, this change requires the presence of a hydroxyl group which can be methylated, for if the wood is methylated with diazomethane before the sulfite treatment, the lignin can no longer be dissolved (cf. p. 212).

b. The Properties of Dissolved Lignosulfonic Acid. B. Tollens and J. B. Lindsey (147) isolated the lignosulfonic acid as the lead salt, or by precipitation with alcohol. These methods do not permit the preparation of the pure substance, since other acids present in the sulfite waste liquor also precipitate. P. Klason (148) later attempted to salt out the lignosulfonic acid with calcium chloride, but he obtained only half of the lignin by this

procedure, the other half remaining in solution. He therefore assumed that the lignin was not a uniform substance. The partial precipitability of the lignosulfonic acid was later confirmed by K. Melander (149). From his figures it can be calculated that only 37% of the lignin present is precipitated with sodium chloride. This lignin was called α -lignin, while that which could not be salted out was designated as β -lignin. Fractional precipitation of the α -lignosulfonic acid with hydrochloric acid gave lignosulfonic acid preparations with widely varying ratios of carbon to sulfur. In Melander's opinion there exists a mixture of similar sulfonic acids.

M. Hönig and J. Spitzer (150) treated concentrated sulfite waste liquor with sulfuric acid, then converted the sulfonic acids which precipitated into the barium salts, and fractionally precipitated the barium salts with alcohol. Four fractions were analyzed. The first three had compositions which agreed only approximately, while the fourth differed markedly from the other three; according to P. Klason, this was probably due to the splitting off of methyl alcohol or formic acid during the cooking. The compositions of the first three fractions of Hönig and Spitzer agreed fairly well with that of a salt investigated by Klason.

The use of certain aromatic amines to precipitate lignosulfonic acid, first discovered by H. R. Procter and S. Hirst (151), has considerably extended our knowledge of the composition and properties of this acid. P. Klason (152) was the first to study this reaction closely. According to Klason's theory, the portion of the " α -lignin" which reacts with sulfites is an acrolein residue, which combines in the following way:



Sulfurous acid or sulfite is also bound "reversibly" to the aldehyde group, but if the reversibly bound sulfite is removed, the salts of aromatic amines in acid solution can cause yellow precipitates to form. Klason supposed that it is most logical to assume that these precipitates are the normal amine salts of the lignosulfonic acid. On the other hand, the fact that Klason was unable to remove all the naphthylamine from the β -naphthylamine compound with alkali seemed to justify the assumption that the naphthylamine is joined to the aldehyde group, forming an azomethine compound (Schiff's base).

This assumption was also supported by the fact that when the naphthylamine compound was dissolved in alcohol and treated with calcium carbonate, it gave a compound which corresponded approximately to the formula $\text{C}_{60}\text{H}_{56}\text{O}_{16}\text{S}_2\text{N}_2\text{Ca}$ (153).

K. Melander found, however, that a toluidine precipitate of lignosul-

fonic acid could be determined by titration with alkali and phenolphthalein just as accurately as aniline hydrochloride. He therefore assumed that the amine compounds were simply normal salts (154).

It is a fact, however, that part of the amine can not be set free by alkali; it is impossible, therefore, that a simple salt formation occurs exclusively. It is fairly certain that azomethines or other condensation products also are formed (155). (Cf. also the color reactions of lignin with aromatic amines, p. 182-193).

The α - and β -naphthylamines were formerly quite widely used as precipitating agents. They do not give complete precipitation of the lignosulfonic acid. P. Klason (152) has designated the precipitable part as α -lignin and the remainder as β -lignin. These fractions are *not* identical, however, with those obtained by precipitation with sodium chloride. Naphthylamine precipitates a considerably larger amount of lignosulfonic acid than does sodium chloride (156).

As far as the cause of the precipitability is concerned, P. Klason (157) assumed that it was due to the aldehydic nature of the α -lignin. According to him, the non-precipitable β -lignosulfonic acid contained a carboxyl group instead of an aldehyde group.

It was found, however, that the precipitability depended on the conditions during the sulfite cooking (156). For example, if the cooking was carried out with sulfurous acid, instead of with the considerably less acid bisulfite solution, a waste liquor was obtained from which almost all of the lignosulfonic acid could be precipitated with naphthylamine. Lignosulfonic acid which had been purified by dialysis could likewise be completely precipitated. It was thus made evident that the precipitability had some connection with the *particle size* of the lignosulfonic acid. The precipitation with aromatic amines could be compared with the well-known salting-out procedures.

Attempts at precipitation with quinoline (158) gave smaller amounts of precipitable acid. On the other hand, T. Hennig (159) showed that after precipitation with naphthylamine, further quantities of lignosulfonic acid could be precipitated with fuchsin. A. Noll (160) has tested several bases of higher molecular weight belonging to different groups of dyestuffs, as azines, xanthenes, acridines and indocyanines, and found that trypaflavine (3,6-diamino-10-methyl-acridinium chloride) was a rather sensitive precipitant for lignosulfonic acid. The best results were obtained with an antiseptic base, "surfen," [bis-(2-methyl-4-amino-6-quinoly)carbamide]. Lignosulfonic acid in a dilution of 1 : 160,000 still gives a slight precipitation with this reagent, and a ten times more dilute solution still produces a just detectable turbidity. W. Lautsch and G. Piazzolo (106 b)

used 3,4-benzacridine, which caused a nearly quantitative precipitation of lignosulfonic acids from sulfite waste liquors. Crude high-boiling fractions of coal-tar bases had a similar effect.

H. Erdtman (161) investigated the precipitation with a series of bases, and found that the molecular size of the base has a certain influence. N,N-Dimethylaniline is not suitable, because of its poor precipitating power, but condensation of the dimethylaniline with formaldehyde yields 4,4'-bis(dimethylamino)diphenylmethane, which has more than twice as high a molecular weight and which is a fair precipitating agent. Quinoline is also fair, but it is not nearly so good as 6,6'-biquinoline sulfate. Bases with excellent precipitating power are β -naphthylamine, strychnine (brucine) and β -naphthoquinaldine.

It has already been pointed out that the quantity of precipitable lignosulfonic acid depends not only on the precipitating agent, but also on the manner in which the cooking is conducted. The following table gives some data on the precipitability of various commercial waste liquors from the pulping of spruce wood:

Precipitating Agent	Per Cent of the Methoxyl Content Precipitated from the Waste Liquor	
	Rayon Pulp	Strong Sulfite Pulp
4,4'-Bis(dimethylamino)diphenylmethane . . .	73	57.5
Quinoline	77	63.5
β -naphthylamine	85.5	77.5
Strychnine	87.5	84
6,6'-Biquinoline	88	88
β -Naphthoquinaldine	92	88.5
Basic lead acetate	98.5	98.5

It should be noted that basic lead acetate, as well as many of the bases mentioned, precipitates not only the lignosulfonic acid, but also materials derived from the sugars, like aldonic acids. It is nevertheless true that a small amount of the methoxyl of the wood remains in solution. This methoxyl is bound to sugar components.

It has already been pointed out that P. Klason designated the lignosulfonic acid which was not precipitated with naphthylamine as β -lignosulfonic acid. He thought that the precipitability was due to the presence of an aldehyde group, and he therefore assumed that the β -acid had a carboxyl group instead of an aldehyde group. Hence he undertook to isolate the β -acid with lead acetate. It is not surprising that besides the sulfonic acid groups, he obtained carboxyl groups belonging to co-precipitated aldonic acids (cf. Chapter V, p. 431).

Larger or smaller quantities of lignosulfonic acid can be obtained by precipitation of sulfite waste liquors with various organic bases. E. Hågg-lund and T. Johnson (162) precipitated with α -naphthylamine, thus

removing the " α -lignosulfonic acid." The acids which had not separated were precipitated as barium salts by means of alcohol, and separated from carboxylic acids (aldonic acids, etc.) by treatment with the calculated quantity of sulfuric acid. The " β -lignosulfonic acids" obtained in this way had an exceptionally high sulfur content and a low methoxyl content. They reduced Fehling's solution more strongly than did the " α -lignosulfonic acid."

The fractionation of the sulfonic acids was recently extended by Erdtman (163), working in Häggglund's institute. He fractionated waste liquors from the preparation of rayon pulp and strong pulp, first by precipitation with 4,4'-bis(dimethylamino)diphenylmethane, then with brucine, and finally with basic lead acetate or alcohol. All of the sulfonic acid fractions were isolated as barium salts, and freed of carboxylic acids by means of sulfuric acid. H. Erdtman, P. Ericson, and E. Häggglund (164) isolated the corresponding fractions of a waste liquor obtained by pulping spruce wood with 12% sodium bisulfite solution (pH 4 at room temperature).

Sixty to ninety % of the lignosulfonic acids precipitated with 4,4'-bis(dimethylamino)diphenylmethane. The precipitated acids behaved like typical α -lignosulfonic acids; they were, for example, practically undialyzable. The brucine fractions were transitional compounds to those isolated with alcohol or lead acetate, and were partly dialyzable. The compositions of the sulfonic acids from the various waste liquors are compared in the following table:

Waste Liquor	Fraction	Empirical Formula	Copper Number	
			Before Hydrolysis	After Hydrolysis
Rayon pulp.....	4,4'-Bis(dimethylamino)diphenylmethane	$C_9H_{9.5}O_{2.6}(OCH_3)_{1.0}(SO_3H)_{0.4}$	8.3	7.7
Strong pulp.....	Ditto	$C_9H_{8.9}O_{2.4}(OCH_3)_{1.0}(SO_3H)_{0.5}$	1.4	1.4
NaHSO ₃ cook...	Ditto	$C_9H_{9.8}O_{2.4}(OCH_3)_{1.0}(SO_3H)_{0.5}$	0	3.4
Rayon pulp.....	Brucine	$C_9H_{10.6}O_{3.2}(OCH_3)_{0.9}(SO_3H)_{0.6}$	6.5	11.3
Strong pulp.....	"	$C_9H_{9.1}O_{2.6}(OCH_3)_{1.0}(SO_3H)_{0.6}$	2.8	5.5
NaHSO ₃ cook...	"	$C_9H_{9.1}O_{2.7}(OCH_3)_{1.0}(SO_3H)_{0.7}$	0	1.6
Rayon pulp.....	Alcohol	$C_9H_{11.6}O_{4.0}(OCH_3)_{0.7}(SO_3H)_{0.9}$	16.4	18.4
Strong pulp.....	"	$C_9H_{13.2}O_{5.7}(OCH_3)_{0.5}(SO_3H)_{0.8}$	12.0	36.5
NaHSO ₃ cook...	"	$C_9H_{14.8}O_{8.4}(OCH_3)_{0.4}(SO_3H)_{1.0}$	11.0	87

It will be seen that the " α -acids" contain about 1S to 20C (2 methoxyls). The sulfonic acids of lower molecular weight contain more sulfur and less methoxyl. The reason for this is not yet fully understood. In this connection, the reducing power of the acids before and after hydrolysis is of interest; these data are given in the last columns.

The lignosulfonic acids of high molecular weight have low copper numbers, which increase only slightly on hydrolysis. It is quite certain, therefore, that they contain no carbohydrates which are bound as gluco-

sides; their elementary compositions (after the sulfonic acid groups have been subtracted) are in agreement with this result, for they are very close to that of lignin. [Cf. A. Larsson (165) for figures on aspen wood.]

The sulfonic acids of low molecular weights have higher copper numbers; the highest are found in the waste liquors from the manufacture of rayon pulp. The increase in the copper number is greater, the lower the copper number was before hydrolysis (i.e., the milder the cooking). This might indicate that these lignosulfonic acids contained increasing amounts of glucosidic carbohydrates. It was actually possible to demonstrate that the hydrolyzate of the sulfonic acid fraction precipitated with alcohol from sulfite waste liquor contained mannose (166). The low-molecular sulfonic acids, especially those obtained by alcohol precipitation after a previous brucine precipitation, are not uniform, however; this fact was demonstrated by fractionation of the acids after methylation with diazomethane (167).

It is possible that these fractions are mixtures of lignosulfonic acids of very low molecular weight with other sulfonic acids, like the sugar sulfonic acids, perhaps polysaccharide sulfonic acids [cf. also E. Adler (168)]. This would explain the fact that their composition differs so widely from that of ordinary lignin, especially in having a high oxygen and a low methoxyl content.

On the basis of these results it is easy to understand why such widely varied values are obtained when the *molecular weight* of lignosulfonic acid is determined. Part of the lignosulfonic acid in the sulfite waste liquor, the " β -acid," with a high sulfur content, has a lower molecular weight, and partly dialyzes through parchment membranes. P. Klason (78) attempted to determine the molecular weights of the barium and calcium salts of lignosulfonic acid by measuring the depression of the freezing point; he obtained values of 2,000-6,000. Ebullioscopic determinations of the molecular weight of the calcium salt gave values of 901 and 1,060. Klason attributed the much higher values obtained by the cryoscopic method to the tendency of the lignosulfonic acid to associate. He assigned a molecular weight of 714 to the lignin itself.

K. Melander (149) obtained values between 822 and 991 by the cryoscopic method, and O. Borodina (169) reports 527 for the result of a soft cook, and 433 from a hard cook.

K. Schwabe and L. Hasner (170) also determined the molecular weight of lignosulfonic acids by means of a dialysis method due to H. Brintzinger (171), G. Jander and H. Spandau (172), and H. Spandau and W. Griess (173). In these experiments lignosulfonic acids precipitated with fluorosilicic acid according to G. Racky (174), or with β -naphthyl-

amine, according to Klason have been studied. In the first case values lying between 5,000 and 19,000 were obtained, while in the second case the value was about 4,000. Direct dialysis of sulfite waste liquor gave fractions containing 7% of sulfur, 10.1% of methoxyl, and having an average molecular weight of 325. These fractions were obtained in yields of about 12% of the lignin. A smaller, non-dialyzable fraction had a molecular weight of 20,500. It was low in sulfur (4.8%), but had a normal methoxyl content (13.4%). Most of the acid was contained in intermediate fractions with molecular weights between 324 and 1,745.

D. Pennington and D. M. Ritter (175) determined the particle size of lignosulfonic acids in sulfite waste liquor, using a cell with pyrex glass diaphragms. They obtained higher values for the bulk of the material than those found previously, viz., 3,000-10,000 or more. Values of the same order of magnitude have been obtained by F. M. Ernsberger and W. G. France (175 a).

N. J. Ögland (176) has studied the purification of the high molecular part of lignosulfonic acids in sulfite waste liquor by continuous dialysis, and similar experiments have recently been described by Q. P. Peniston and J. L. McCarthy (106 c). These authors found that about 65-80% of the total lignosulfonic acids (calculated on the basis of the methoxyl content) is non-dialyzable. Such high-molecular lignosulfonates from two different sulfite waste liquors (A and B) had the following empirical compositions, calculated on a sulfur-and ash-free basis:

Sample A.....	$C_{9.00}H_{7.20}O_{2.75}(OCH_3)_{0.94}$
Sample B.....	$C_{9.00}H_{7.00}O_{2.84}(OCH_3)_{0.95}$
"Theoretical"...	$C_{9.00}H_{7.00}O_{2.75}(OCH_3)_{1.00}$

The "theoretical" ratio given has been based on the assumption that the lignin consists of "*n*" guajacyl propane structural units with the empirical formula $C_{10}H_{10}O_3$ and "*3n*" units with the empirical formula $C_{10}H_{10}O_4$.

Experimental details for the separation of lignosulfonic acids from sulfite waste liquor by batch dialysis from cellophane bags have been given by N. K. Hiester, J. L. McCarthy, and H. K. Benson (177).

II. Staudinger and E. Dreher (178) investigated the viscosity of sodium lignosulfonate in formic acid, and found a specific viscosity of 0.064 for a 1% solution; according to them, this proves that lignin contains no long-chain molecules (179).

Lignosulfonic acids from spruce, obtained from various sources, and isolated by various procedures, have been studied by several authors. The elementary compositions of the lignins from which the acids were derived varied between 64.7 and 68.1% C, 5.95 and 6.95% H, and 13.27 and 15.85% methoxyl.

New methods of isolating the lignosulfonic acid have, however, meanwhile been worked out, and the deeper understanding of the sulfite cooking process which has gradually been achieved has helped to make it possible to obtain lignosulfonic acids which are known to have been prepared in a manner not injurious to their structure.

The above-mentioned results of K. Freudenberg, W. Lautsch, and G. Piazzolo (118) show that there is a certain difference in the elementary composition of the lignins from which the lignosulfonic acids of the first and last fractions are derived. This is illustrated in the following table:

	C %	H %	OCH ₃ %	O %	OH %	COOH %	Molecular Weight of the Unit
Fractions 1-4 . . .	66.5	6.1	15.7	9.4	9.2	1.8	180
Fractions 5-8 . . .	68.0	6.1	15.8	6.1	10.2	2.8	177
Cuproxamlignin .	66.7	6.2	16.1	10.7	8.4	—	179

About $\frac{1}{5}$ of the total hydroxyl proved to be phenolic. The C : H ratio was about 9 : 11; i.e., between C₉H₁₀ and C₉H₁₂; this was interpreted to mean that the lignins investigated contained both condensed and uncondensed units at the same time. (By uncondensed units are meant those which are bound together only through ether linkages.)

It was doubtful whether lignosulfonic acid contains any *carboxyl groups*. The analyses reported by various authors [cf. H. Erdtman (163)] indicate that the ratio of Ba : S is 2, within the experimental error.

Recently, O. Samuelson and A. Westlin (179 a) measured the amount of sulfonic acid groups in lignosulfonic acids by potentiometric and conductometric titrations. They found that the value obtained was always lower than that which might have been expected from the analytically determined sulfur content of the preparations. In two different lignosulfonic acids only 80% of the total sulfur was present as sulfonic acid groups (179 b). Since no inorganic sulfur was detectable, the "excess sulfur" must be bound to the organic substance. According to a theory of Samuelson and Westlin, this "excess sulfur" originates from a reaction between lignin and thiosulfate formed during sulfite cooking (cf. Chapter V, page 426).

The question then arises how the analytically found ratio Ba : S = 2 can be explained. The potentiometric titration curves of lignosulfonic acids showed a considerable buffering capacity between pH 5 and 8, in contrast to the titration curves of other low or high molecular organic sulfonic acids which gave a normal, sharp potential change at the equivalence point (179 c). According to Samuelson, this indicates that there is an appreciable amount of carboxyl groups present in the lignosulfonic acid. In order to explain the equivalence of Ba and S in lignosulfonates,

one must assume that the amount of carboxylic acid groups is approximately equivalent to the amount of "excess sulfur".

Treatment of the free lignosulfonic acid with 4% *hydrochloric acid in methyl alcohol* caused the methoxyl content to increase from 14.4% to 16.8% (180). C. Kullgren (141) had earlier found that alkoxy groups were taken up when free, solid lignosulfonic acid was extracted from bisulfite-treated wood with alcohol. These alkoxy groups are split off again on treatment with acetic acid containing HCl (181). According to Freudenberg, this behavior is characteristic of alkoxy groups of the acetal type. It should be pointed out, however, that alkoxy groups, which are bound in the form of benzyl ethers, would behave in a similar way (cf. p. 203 and p. 210).

Concerning the behavior of lignosulfonic acid toward *halogens*, it may be mentioned that B. Tollens and J. B. Lindsey (182) found that lignosulfonic acid reacted with bromine to form an insoluble compound containing 4Br and 1S for each C_{26} residue. H. Krause (183) later found that lignosulfonic acid gave a substance with the composition $C_{26}H_{29}O_{12}ClS$ when it was treated with bleaching powder in hydrochloric acid solution. P. Klason (184) found that barium lignosulfonate took up 2 atoms of iodine to form a substance with the empirical formula $C_{40}H_{44}I_2S_2Ba$; it was therefore concluded that the salt contained a double bond. Dorée and Hall (185) reported that when lignosulfonic acid was dissolved in acetic acid it could add 2.9 atoms of bromine for every sulfur atom present. A. W. Karatejew (186) found that methoxyl groups were split off during chlorination, and that more methoxyl was split, the more chlorine was taken up. The sulfonic acid groups were not all split. J. H. Pedersen and H. K. Benson assert (187) that the sulfonic acid groups are not removed to any appreciable extent by chlorine.

R. S. Hilpert (188) has carried out extensive investigations of the properties of chlorinated lignosulfonic acids. Lignosulfonic acid can take up as much as 30% of chlorine. Chlorate-hydrochloric acid solutions can be advantageously used as reagent. Products are obtained in this way which, according to Hilpert, can be used without further additions to tan a usable leather; they are said to be equal to the vegetable tanning agents, such as quebracho. However, chlorinated lignosulfonic acid has not proved suitable for commercial tanning, allegedly because hydrogen chloride is split off to some extent, and destroys the leather. Hilpert supposes that chlorination of lignosulfonic acid results in the formation of chlorinated quinones. Chlorination also results in the splitting of some sulfonic acid groups; this causes a reduction in the water-solubility. When sulfite waste liquor is treated with chlorine at room temperature and subsequently

heated to 110-170° C. the lignin products become insoluble (188 a). According to Hilpert, chlorinated lignosulfonic acid should be given consideration as a disinfectant.

A removal of 50% of the total sulfur by bromination of lignosulfonic acid has been reported by K. Kratzl and C. Bleckmann (189). In model experiments it was shown that Na propioguuaiacone- α -sulfonate loses its sulfo group when treated with an excess of bromine.

K. Schwabe and E. Preu (190) have added thiocyanogen to lignosulfonic acid by electrolytic methods, and have precipitated the acids formed with alcohol. Ethanol precipitates 60-65% of the acids, methanol 40%, and butanol practically all of them. The sulfur content of the products is near to the limiting value of 16.5%. It is assumed that one hydrogen atom of each benzene nucleus is replaced by a thiocyanogen group. The introduction of cyanogen and azide groups into the lignosulfonic acid has, so far as is known, not yet been investigated.

Attempts have also been made to *nitrate* lignosulfonic acid. C. Dorée and L. Hall (185) nitrated with 5% nitric acid, which split off the sulfonic acid group and gave a product containing 1.2% of N. J. S. Carpenter and H. K. Benson (191) found that lignosulfonic acid was easily nitrated only after treatment with alkali, which split off the sulfonic acid groups. The nitrogen content of the product was 4%, which is practically the same as that of nitrated butanol lignin. Treatment with concentrated nitric acid gave oxalic acid in 28% yield (192).

The tanning properties of lignosulfonic acid treated with nitrogen oxides or with nitric acid were found by R. S. Hilpert (188) to be better than those of untreated lignosulfonic acid.

Esters have been prepared by the action of fatty acid chlorides on sodium lignosulfonate [D. K. Longley (193)]. The stearic and oleic esters have been proposed as emulsifiers and for lubrication purposes, as in rayon knitting.

Several investigators have established the fact that protocatechuic acid is formed, among other things, when lignin is degraded by *caustic fusion* (194). K. A. Melander (195) has investigated the action of fused alkali on lignosulfonic acid, and identified the products. Besides the protocatechuic acid, vanillic acid, acetic and higher fatty acids, and 10% of pyrocatechol were obtained. M. Hönig and W. Fuchs (196) carried out caustic fusions of the various fractions of lignosulfonic acid which were obtained by the method of Hönig and Spitzer. Between 13 and 19% of the lignin was obtained in the form of protocatechuic acid. When the alkali fusion of the lignosulfonic acid was carried out in a nickel crucible in an atmosphere of hydrogen, E. Heuser and A. Winsvold (197) found

that 16% of crude protocatechuic acid (corresponding to 12.4% of the purified product) was obtained. There were simultaneously formed 8.8% of crude pyrocatechol (4.4% of pure material) and a little oxalic acid.

Melander was able to demonstrate the presence of adipic acid as a degradation product after lignosulfonic acid had been heated to 360°C under 230 atm. pressure in *alkaline solution*.

If hot sulfite waste liquor is treated with lime, according to the procedure of A. Frank (198) and V. B. Drewsen, organically-bound SO_2 is removed. P. Klason (199) was able to split off only 75% of the sulfur by heating lignosulfonic acid with an excess of baryta. He presumed that the remaining 25% was more firmly bound. The portion which was split by alkali was, in his opinion, probably bound to carbonyl groups. According to later results, this is not correct; at most 10% of the total sulfur can be bound to carbonyl groups (E. Adler and S. Häggroth, unpublished).

M. Hönig and W. Fuchs (200) have made more detailed studies of the splitting of lignosulfonic acid with baryta. Various fractions of lignosulfonic acid, on cooking with baryta, gave a baryta-soluble substance as well as a substance insoluble in water or baryta. The soluble substance was the salt of an acid with the composition $\text{C}_{16}\text{H}_{27}\text{O}_4(\text{CH}_3\text{O})(\text{COOH})(\text{SO}_3\text{H})$, which behaved like a tannic acid.

Other experiments of M. Hönig and W. Fuchs (196) indicated that part of the sulfur in lignosulfonic acid is tenaciously retained during fusion with potassium hydroxide. Only 70% of the total sulfur was split off at a temperature of 250°C. K. Melander (195) found, however, that practically all the sulfur was split on alkali fusion at the same temperature.

G. H. Tomlinson and H. Hibbert (201), too, have found that part of the sulfur is stubbornly retained when lignosulfonic acid is heated with alkali; this seems to indicate that the sulfur is bound to the lignin in at least two different ways.

I. A. Pearl and H. K. Benson (202) found that the sulfur could be completely split under the following conditions: temp., 175-180°C; time, 2 hours; alkali concentration, 35-40%; ratio of lignosulfonic acid to NaOH, 1 : 1. With lime it was also possible to achieve a complete splitting of the sulfur in 2-4 hours at the same temperature and with the same ratio of lignosulfonic acid to lime (concentration of lime, 10-15%) (203).

According to Q. P. Peniston and J. L. McCarthy (203a), mild alkaline hydrolysis of high-molecular lignosulfonic acids results in the formation of weakly acidic groupings, which show a pK value of about 9. They were believed to be phenolic hydroxyl groups. From their experiments, Peniston and McCarthy concluded that 0.67 moles of phenolic hydroxyl per mole of methoxyl are liberated when lignosulfonic acid is

treated in a 5% NaOH solution at 100°C for two hours. Prolonged treatment causes only a very slow further increase in the amount of weak acid groups. Simultaneously with the liberation of phenolic hydroxyls, part of the original sulfur is removed and lower-molecular, dialyzable breakdown products are formed.

V. Grafe (204) was the first to prepare *vanillin* by treatment of sulfite waste liquor with lime at 180°C, and extraction of the reaction products with ether, but his yields were low. K. Kürschner (205) found that vanillin was formed if sulfite waste liquor was boiled with sodium hydroxide while a current of air was being passed through. He determined the vanillin colorimetrically. M. Hönig and W. Ruziczka (206) also heated the waste liquor with sodium hydroxide, and determined the vanillin gravimetrically, according to J. Hanuš' *m*-nitrobenzoic acid hydrazide method (207). They established the fact that the yield of vanillin was dependent on the manner in which the sulfite cooking had been conducted. The way in which the alkali treatment was carried out also had an important effect on the yield. The highest yields of vanillin were obtained when 1 liter of waste liquor was heated to 160-170°C with 100 g. of sodium hydroxide; the yield was then 1-2.4 g. per liter. Passing air through the solution had an adverse effect on the yield. K. Kürschner and W. Schramek (208) investigated this problem systematically, and were able to increase the yield to 3.2 g.

G. H. Tomlinson and H. Hibbert (201) have made a thorough study of the formation of vanillin. They determined the effect of the alkali concentration and the reaction time on the yield, as well as the way in which the yield varied with the conditions in the sulfite cooking. Certain indications were observed that the vanillin yield increased with the sulfur content of the lignin. The lignosulfonic acid was also fractionated by adding sodium chloride, giving " α -acids I and II"; what did not precipitate was thrown down by lead salts, giving a " β -acid." The yield of vanillin obtained from the various fractions by heating with 24% sodium hydroxide solution for 12 hours was determined, with the following results:

Fraction	% Lignosulfonic Acid Precipitated	% S in the Ca-Free Substance	% CH ₃ O in Substance Free of CaHSO ₃	% Vanillin Referred to Lignin
α -Acid I.....	19	9.7	15.4	6.1
α -Acid II.....	44	10.0	15.8	6.6
β -Acid.....	37	11.0	15.2	8.4

When the lignosulfonic acid was methylated, and then cleaved with alkali under mild conditions, veratraldehyde was obtained. With stronger alkali this aldehyde undergoes a Cannizzaro reaction, being converted to the corresponding alcohol and carboxyl acid.

The formation of veratraldehyde shows that the original lignosulfonic acid contains free phenolic hydroxyl groups. According to Hibbert, the same phenolic groups are present in the same quantities in other lignin preparations, and are not formed by the sulfonation process.

According to Freudenberg (p. 225) and Peniston and McCarthy (109 c) the amount of free phenolic hydroxyl groups in the original lignosulfonic acid is very low. Freudenberg gives a value of about 0.25 mole, Peniston and McCarthy < 0.2 mole per mole of methoxyl.

Tomlinson and Hibbert suggested that part of the sulfite is bound as in compound I:



When compound I is heated with alkali, it forms II. This is an aldol, from which, according to Hibbert, vanillin might be formed by a "reversed aldol condensation" (cf. p. 232).

Investigations of E. Hägglund and L. C. Bratt (209), and of O. Alvfeldt (210) have shown with certainty that the yield of vanillin increases proportionally to the sulfur content. This is true not only for lignosulfonic acid in solution, but also for solid lignosulfonic acid. The following figures may be quoted:

Lignosulfonic Acid Preparation	Sulfur Content	Yield of Vanillin in % of the Original Lignin
Solid lignosulfonic acid, Ca salt.....	4.45	3.0
" " " " " "	4.6	3.5
" " " " " "	5.95	4.8
Dissolved lignosulfonic acid, Na salt.....	3.74	2.2
" " " " " "	5.12	3.1
" " " " " "	6.82	4.2
" " " " " "	7.59	4.8
" " " " K salt.....	5.79	3.9
" " " " " "	6.65	5.0
" " " " Ca salt.....	7.54	5.3
" " " " " "	9.62	6.8

These results have not yet been explained satisfactorily on the basis of the chemistry of lignin. It may be assumed that sulfonation causes a rearrangement in the side chain of the lignin, resulting in the formation of some grouping which, on alkali treatment, yields vanillin (cf. p. 232).

This grouping seems to be very susceptible to self-condensation, which reduces or prevents the formation of vanillin. The experiments of E. Hägglund and H. Heiwinkel (211) quoted below seem to support this assumption. Waste liquor from a hard cook was heated for various lengths of time at 140 C with a bisulfite cooking acid containing 1% CaO and 5.5%

SO₂. The liquors were then neutralized, and the vanillin produced by the method of Tomlinson and Hibbert. The following results were obtained:

Expt. No.	Cooking Time hours	Vanillin, in % of Lignin Used	Color of the Liquor
1.....	0	5.0	yellow
2.....	0.5	4.6	"
3.....	1	4.7	"
4.....	2	5.0	"
5.....	3	3.4	brown
6.....	3.5	0	very dark brown
7.....	4	0	" " "
8.....	5	0	" " "

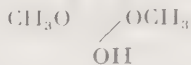
It is apparent from these experiments that the lignosulfonic acid of the liquor is so altered by overcooking (or burnt cook) that it finally no longer yields any vanillin on treatment with alkali.

The yield of vanillin is also decreased by treatment of the lignosulfonic acid with mineral acids of the same strength as that present at the end of a sulfite cook. An α -lignosulfonic acid, for example, from which 4.3% of vanillin could be obtained, yielded only 2.5% of vanillin after it had been heated to 135°C for 2 hours with 0.02 N sulfuric acid.

In addition to vanillin, H. Hibbert, I. K. Buckland, G. H. Tomlinson, and F. Leger (212) have found acetoguaiacone (acetovanillone)



in small yields, amounting to 0.2-0.3% of the lignin, when the lignosulfonic acid from conifers was degraded with alkali. Alkali degradation of lignosulfonic acid from yellow birch yielded, besides vanillin, quantities of syringaldehyde equal to 2.9% of the weight of the lignin (213).



Small amounts of acetosyringone were also isolated.

Appreciably higher yields of vanillin can be obtained when lignosulfonic acid is *oxidized* with *nitrobenzene* in *alkaline solution*.

K. Freudenberg, W. Lautsch, and K. Engler (214) have demonstrated that in the presence of nitrobenzene vanillin is obtained not only from sulfite waste liquor, but also from isolated lignin and from the wood itself. The reaction was carried out at 160 C in the presence of nitrobenzene and alkali in an autoclave, with stirring. The yield of vanillin

from cuproxam or hydrochloric acid lignin, or from lignosulfonic acid is about 20%. Even higher yields, running up to 25%, are obtained from the spruce wood itself.

As in the non-oxidative vanillin formation by treatment with alkali described above, the yield of vanillin increases with increasing degree of sulfonation in the nitrobenzene-alkali-oxidation (109 b), too.

W. Lautsch, E. Plankenhorn, and F. Klink (215) found that lignosulfonic acid gave considerably more vanillin when it was heated under pressure with oxygen in alkaline solution than when it was heated without oxygen. The following example may be quoted:

Four hundred cubic centimeters of waste liquor, containing 11 g. of lignin and 48 g. of sodium hydroxide, was heated with stirring to 110°C in an autoclave.

Treatment	Pressure atm.	Duration of Treatment, hrs.	Yield of Vanillin in % of Lignin
Gas space filled with N ₂	—	5	3.1
Air passed through at 5 atm.....	5	5	5.3
Oxygen passed through at 5 atm..	5	5	8-9

The yield of vanillin proved to be quite dependent on the concentration of alkali. For example, when 48 g of NaOH were added to 400 cc. of waste liquor under the conditions given above, the yield of vanillin amounted to 8-9% of the weight of the lignin; with 20 g. of NaOH, it was 6%, and with 10 g. only 1.2%. It was possible to work with small amounts of alkali if the temperature was raised and the time of the reaction shortened. The use of cobaltic hydroxide as a catalyst did not give appreciably higher yields. The yields were at best only a third of those obtained by oxidation with nitrobenzene.

By studying the behavior of simple model substances, A. v. Wacek and K. Kratzl have tried to get information about the mechanism of vanillin formation by both non-oxidative and oxidative (nitrobenzene) alkaline treatment of lignosulfonic acid.

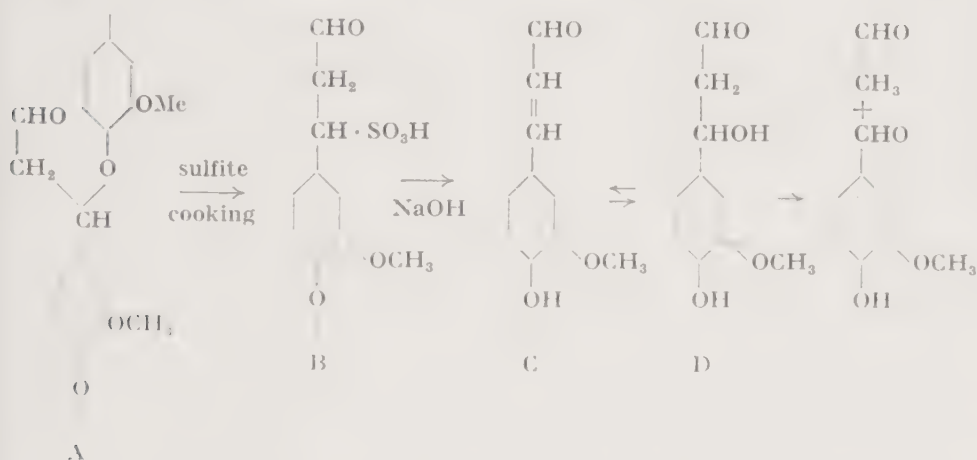
Concerning the non-oxidative process, they found that from a great number of models (216 a-d) only substances belonging to the types:



were broken down by boiling 24% NaOH into the corresponding aromatic aldehydes (216 e-g). Typical examples of such substances were the chalcones [cf. also Tomlinson (216 h)] and cinnamaldehyde, as well as their corresponding hydrosulfonic acids. The structural specificity of aldehyde formation thus demonstrated seemed to give strong support to the idea

of Hibbert (cf. page 230), that the non-oxidative vanillin formation from lignosulfonic acid is the result of a "reversed aldol condensation." From the types of substances mentioned above aldols are derived by addition of H_2O to the $C=C$ bond or by hydrolytic removal of the sulfo group, respectively.

Slightly later, Kratzl (216 i-l) made the important observation, that alkaline degradation of lignosulfonic acid yielded acetaldehyde in addition to vanillin. Since cinnamaldehyde or cinnamaldehyde hydrosulfonic acid on similar treatment also yield acetaldehyde (in addition to benzaldehyde), Kratzl assumed that lignosulfonic acid contains groups of the structure B, i.e., coniferaldehyde hydrosulfonic acid groups. Under the influence of boiling alkali, the sulfo group should be split off, yielding coniferaldehyde (C) and the corresponding aldol (D), which may be broken down to acetaldehyde and vanillin.



According to Kratzl, group B may arise during the sulfite cooking process from ether-linked units (A), occurring in the original lignin of the wood.

The alkaline fission of free coniferaldehyde and its hydrosulfonic acid into acetaldehyde and vanillin has been demonstrated by E. Adler and S. Häggroth (216 m).

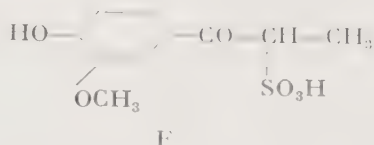
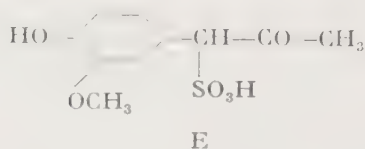
Kratzl's formulation, however, does not account for the fact disclosed by Tomlinson and Hibbert (201) that the vanillin-yielding units in lignosulfonic acid are phenolic (cf. page 230). Furthermore, Adler and Häggroth showed that the amount of groups (B) present in lignosulfonic acid (cf. p. 190) is much too low to explain the vanillin and acetaldehyde yield actually obtained. Lignosulfonic acids from hard pulp waste liquors, for instance, contained only 1 group (B) for each 50 OCH_3 groups, while the yield of aldehydes on alkaline hydrolysis amounted to 1 vanillin per 12-15 OCH_3 and 1 acetaldehyde per 9-12 OCH_3 . Ligno-

sulfonic acids from rayon pulp waste liquors, which gave similar yields of fission aldehydes, contained practically no coniferaldehyde systems at all.

On the other hand, it could be shown that not only the yield of vanillin (cf. page 230) but also of acetaldehyde increases with increasing degree of sulfonation, and furthermore, that during the course of the alkaline heating, the acetaldehyde formation runs parallel to the formation of vanillin (216 n). Thus, it is obvious, that both aldehydes originate from the same fission reaction. It seems probable that the coniferaldehyde structure is an intermediate step in this reaction. However, the structure of those units in the lignosulfonic acid molecule which, under the influence of boiling alkali, give rise to the intermediate coniferaldehyde structure is still obscure. It cannot be identical with structure B.

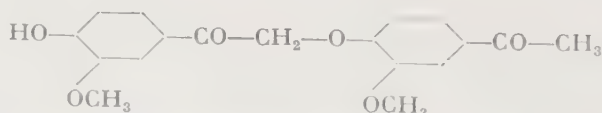
In contrast to previous statements (216 g), Adler and Häggroth (216 m) found that the original lignin in the wood also yields vanillin on non-oxidative alkaline heating. Acetaldehyde is also liberated in this case. The yields of both aldehydes are, of course, much lower than those obtained from lignosulfonic acids; they correspond, however, approximately to the amount of coniferaldehyde groups present in the wood, i.e., about 1 coniferaldehyde group for each 40-60 methoxyl groups (E. Adler and L. Ellmer, cf. page 190).

The oxidative alkaline vanillin formation, for example in the presence of nitrobenzene, seems to be of much less structural specificity than the non-oxidative process (216 o, 217, 218). All guajacyl-propane derivatives studied yielded vanillin, in varying amounts. For example, the sulfonic acid models E and F, which correspond to Hibbert's alcoholysis products (cf. page 241),



did not give any vanillin with alkali alone, but yielded 15 and 31 %, respectively, of the theoretical amount, when heated with alkali and nitrobenzene. The presence of the phenolic hydroxyl group in *para*-position proved to increase the aromatic aldehyde yield on alkaline oxidation.

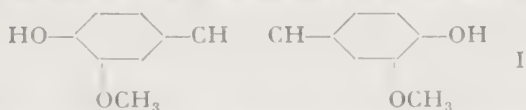
H. Erdtman and B. Leopold (117) reported that a model substance of the structure



yielded vanillin on oxidation with nitrobenzene and alkali.

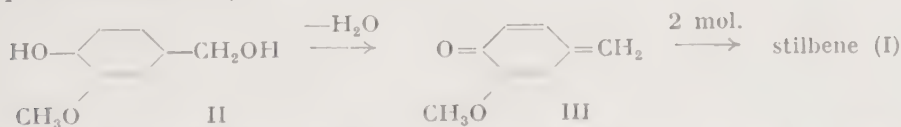
I. A. Pearl (219) studied the oxidation of basic calcium lignosulfonate by means of mercuric oxide or silver oxide in the presence of an excess of sodium hydroxide in water solution. On boiling the mixture under reflux, a degradation of the lignosulfonic acid took place and ether soluble products were formed in yields ranging from 40-55% of the original lignin. The chief products were vanillic acid and vanillin. Other compounds isolated were guaiacol and acetoguaiacone, and, when mercuric oxide was used as the oxidant, 5-hydroxymercurivanillin.

In this connection it should be mentioned that H. Richtzenhain and C. v. Hofe (220) obtained 3,3'-dimethoxy-4,4'-dihydroxystilbene (I)



by heating sulfite waste liquor from spruce according to the G. H. Tomlinson-H. Hibbert procedure (212). The yields were never more than 1% of the lignin. The way in which this substance is formed has not been discussed by these authors; they only state, that it is not to be considered as a secondary product formed from the vanillin which is first produced by the degradation of the lignin.

It seems possible that the stilbene derivative (I) has been formed by some process involving the intermediary formation of the unstable *p*-quinonemethide (III),



which, by analogy with previously known cases (221), would undergo an instantaneous dimerization to the stilbene. The quinonemethide might arise from vanillyl alcohol (II) by dehydration. Similar processes may also explain the formation of the stilbene and dibenzyl derivatives, obtained by H. Richtzenhain (222) on oxygenation of 5-methylpyrogallol 1,3-dimethyl ether.

Oxidation of ammonium lignosulfonate with *periodic acid* has been studied by D. Pennington and D. M. Ritter (223). One mol. HIO_4 was consumed by an equivalent of the weight 525, corresponding to about two methoxyl groups. The oxidized product yielded a barium salt which was sparingly soluble in water and contained 6.4% OCH_3 and 17.2% Ba, whereas the barium salt of the starting material had 10.4% OCH_3 and 12.5% Ba. This indicates, that a methoxyl-containing group has been removed from the lignosulfonic acid. An oxime with 2.7% N was obtained from the oxidation product.

Since substances like guaiacol and vanillic acid consume considerable amounts of periodic acid, it is probable that periodic acid attacks certain aromatic rings in the lignosulfonic acid (224).

Lignosulfonic acid is easily condensed by *heating in acid solution*. This is what occurs in "burnt cook"; this matter will be considered in detail later on (p. 423).

Complete decomposition of the lignosulfonic acid evidently occurs when so-called "sulfite charcoal" is prepared according to the method of R. W. Strehlenert (225). This is accomplished by pressure-heating of unneutralized sulfite waste liquor in the presence of oxygen at 200-210°C. A waste liquor containing 11.6% of solids for example, was heated in this manner for 35 minutes, giving a precipitate amounting to 60.9 g. per liter. So far as is known, no investigations of the composition of this charcoal have been published.

C. G. Schwalbe (226) later investigated this process. He precipitated the lime in the lignosulfonic acid as calcium sulfate, by adding sulfuric acid before the heating. The sulfite charcoal obtained after this pretreatment contained 9-12% of ash; the yield per cu. m. was about 70 kg. of charcoal with a heating value of 4,800 cal. The economic practicability of both the Schwalbe and Strehlenert processes has not been proved in practice.

The procedure of Strehlenert is based upon the tendency of free lignosulfonic acid, mentioned above, to condense and form large complexes. The acid thus becomes insoluble, and finally yields sulfite charcoal, after water and SO_2 have been lost.

W. Lautsch (227) investigated the *hydrogenation of lignosulfonic acid*. At 260°C non-poisonable sulfide catalysts yield chiefly high-boiling, tar-like phenols, containing organic sulfur. Considerably higher yields of distillable degradation products were obtained at 340-345°C; in this case the chief products were five- and six-membered cyclic alcohols, and cycloparaffins. If the hydrogenation of sodium lignosulfonate was carried out over nickel on alumina (Rupe) or over Raney nickel, at a pressure of about 450 atm. and a temperature of 340°C, approximately 45% of the lignin was converted to ether-soluble substances, 75-85% of which constituted a neutral fraction, three-fourths of which was distillable. The lower boiling fractions contained cyclopentanol and 2-methylcyclopentanol, as well as higher homologs of cyclopentanol. The higher boiling fractions also contained ether-like substances. According to Lautsch, the method may become technically important.

Another method of reductive breakdown of lignosulfonic acids is pressure heating with alcohols in the presence of alkali. Under such condi-

tions the alcohol acts as a hydrogen donor and no catalysts are necessary (cf. p. 275). On heating sodium lignosulfonate in a water solution containing 7.9% NaOH and 12.7% ethanol for 12 hours at 340 °C, W. Lautsch and G. Piazzolo (227 a) obtained 86% of the lignin in the form of liquid neutral products. Instead of alcohols, carbon monoxide could also be used as the reducing agent. According to R. Monnberg (188 a), about 50% of a lignin which had been prepared from sulfite waste liquor by desulfonation with lime, was converted into distillable products when the lignin was heated to 350 °C with methanol and lime. Methylation of the aromatic nucleus also seems to take place under these conditions.

When the degradation was carried out with butanol and sodium hydroxide at 270 °C for 2 hours, 32.6% of the sodium lignosulfonate used were converted to catechols and 1.3% to monohydric phenols, according to J. P. Salvesen, R. L. Hossfeld, and R. L. Lovin (227 b).

2. Lignin Preparations Obtained by the Action of Alcohols, Phenols, and Various Organic Acids, Amines, and Hydrazine on Wood or Isolated Lignin

a. Alcoholysis of Wood. Alcohol Lignins. P. Klason (228) was the first to attempt to dissolve lignin with alcohol in the presence of mineral acids. He cooked dry spruce chips for 6-10 hours with ten times their weight of 5% hydrochloric acid in alcohol. Approximately 28-32% of the wood dissolved. Alcohol was evaporated from the solution and a brown precipitate was obtained in an amount equal to 6-7% of the weight of the wood. When this precipitate was dried, a resin partly soluble in chloroform was obtained. Klason believed that the material insoluble in chloroform consisted of "pure lignin." J. Grüss (229) carried out similar experiments some years later. He moistened wood with hydrochloric acid, and then cooked with alcohol. The yield was small. The lignin was then fractionally precipitated with water. One of the fractions so obtained contained a crystalline substance melting at 160 °C.

Similar experiments were made by A. Friedrich and J. Diwald (230). The yield of lignin was about 10% of the weight of the wood, when the preparation was carried out as follows: the spruce sawdust was extracted with benzene-alcohol mixture and then with 5% sodium hydroxide. It was then allowed to stand for 2 days with 17% hydrochloric acid, after which it was cooked for 8-10 hours with 10 times its weight of alcohol; the extract was concentrated, and precipitated with water. The precipitate was easily soluble in alcohol, acetone, ethyl acetate, glacial acetic acid, and other solvents, except ether and benzene. This lignin had different properties from the lignins described above, and was termed "primary

lignin" by Friedrich. It had a composition of 64.2% C, 6.5% H, and 20.9% CH_3O . The methoxyl content was increased to 25.2% by methylation.

B. Holmberg and S. Runius (231) carried out independent investigations of the alcoholysis of wood. These studies were made with a view to determining the form in which lignin is present in wood—i.e., whether it is mechanically included or chemically bound to the carbohydrates. If it is chemically combined, there are two possibilities. The first of these is that it might be found as an ester, in which case the lignin would constitute the acid component. The second possibility would be that glucosidic or acetal linkages existed between the two components of the wood. In the latter case it would not be certain whether the lignin constituted the carbonyl component, and the carbohydrate the alcohol, or vice versa.

Only very small amounts of lignin were isolated by treating wood with alcoholic solutions of sodium hydroxide or sodium alcoholate. The residue was unchanged by this treatment. However, if the wood was immersed in boiling, alcoholic 1 *N* hydrogen chloride, in the presence or absence of water, considerable quantities went into solution. The lignin so isolated appears to have a high content of methoxyl, but it was found that it actually contained both methoxyl and ethoxyl groups. [E. Hägglund and B. Sundroos (232) have shown, however, that spruce lignin contains only methoxyl groups and no other alkoxy residues.] The ethoxyl groups were derived from the alcohol; they could not be saponified, and furthermore, since alcoholate appeared to have no effect on wood, it was concluded that no lignin carbohydrate esters were present in the wood, but rather that the lignin of the wood occurs in the form of acetal compounds with the carbohydrates, the lignin constituting the carbonyl component, and the carbohydrate, the alcohol component. The results of J. Grüss and of A. Friedrich and J. Diwald might also be explained in the light of these conclusions (233).

E. Hägglund and H. Urban (234) have carried out investigations of the action of hot, acidified butyl and amyl alcohols on wood. They were able to confirm the results of Holmberg, and they concurred in his opinion that acetals are probably present. They found, furthermore, that isolated lignin derivatives, like hydrochloric acid lignin, likewise take up alcohol, and thus go into solution (235); the significant observation was also made that the undissolved residue takes up appreciable quantities of alcohol before going into solution. The dissolved material has a higher alkoxy content, however. The lignin takes up the alcohol in gradually increasing quantities, and goes into solution when the alcohol taken up is of the order of magnitude corresponding to formation of a hemiacetal (on the assump-

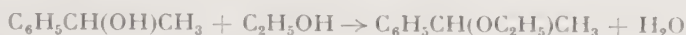
tion of a molecular weight of 400). If this molecular weight is assumed, it turns out that the molecule contains two hydroxyl, two methoxyl, and one carbonyl group. The alcohol lignins have low molecular weights when they are carefully prepared. A. J. Bailey (236) has confirmed this fact for the butyl alcohol lignin prepared from hemlock and aspen; he found values of $420 \pm 14\%$.

The composition mentioned above is in good agreement with the analysis of the ethyl alcohol lignin isolated by B. Holmberg (237) with alcoholic hydrogen chloride. The analysis of this lignin corresponded to a formula of



W. G. Campbell (238) and H. Hibbert and F. E. Brauns (239) later investigated methyl- and ethyllignins. The latter authors come to the conclusion that native lignin can be represented by the formula $\text{C}_{42}\text{H}_{32}\text{O}_6(\text{CH}_3\text{O})_5(\text{OH})_5$. One of the five hydroxyl groups can be methylated with diazomethane, and one with methanol solutions of hydrochloric acid.

The acetal theory, mentioned above, is not the only possible explanation of the formation of alcohol lignins. Another idea has been advanced by B. Holmberg and co-workers (112, 114). They found that α -phenethyl alcohol (cf. p. 202) is converted into its ethyl ether when heated with 1 N ethanolic HCl:



Furthermore, when the ethyl ether was reacted with thioglycolic acid, α -phenethyl thioglycolic acid was formed:



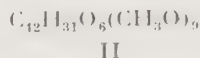
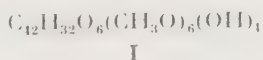
Similarly, when ethanol lignin was treated with thioglycolic acid, the ethoxyl groups were replaced by thioglycolic acid residues (cf. p. 203).

On the basis of these experiments, B. Holmberg concludes that at least one of the reactions leading to the formation of alcohol lignins may be the etherification of a reactive alcoholic group, possibly an aryl carbinol. The alcohol lignins, therefore, may be ethers as well as acetals.

The alcohol lignins are soluble in cold alkali, and are precipitated from the solution by acids, including even carbon dioxide (240). They are not dissolved by sodium bicarbonate (241).

It is certainly quite remarkable that not all of the lignin can be removed from wood with acidified alcohol. One will probably not go far wrong in assuming that condensations of the lignin in the solid phase occur, making the lignin progressively less soluble in the alcohol, as the reaction proceeds. This has been confirmed experimentally by H. Hibbert and H. W. Mac-

kinney (242), who isolated the difficultly-soluble methyl lignin in the wood by completely methylating the wood residue with dimethyl sulfate, and then extracting the carbohydrate with methanol-hydrochloric acid solutions at 100°C. Approximately two thirds of the lignin was thus obtained. The compositions of the soluble methyl lignin I, and of the insoluble, completely methylated methyl lignin II, corresponded to the following formulas:



According to these results, the formation of the insoluble lignin from the native lignin would be accompanied by the loss of one of the ten hydroxyl groups of the molecule.

Y. Hachihama and H. Saegusa (243) achieved a fractional extraction of the lignin from bagasse by heating to 180°C for two hours in slightly aqueous alcohol solutions. The various fractions did not differ markedly in composition.

A. Bailey (244) prepared butyl alcohol lignin by heating wood with butyl alcohol, with or without the addition of alkali. Extensive delignification occurred, when aspen wood was treated for several hours with aqueous butanol (1:1) at 158°C [cf. also H. Y. Charbonnier (245)]. Hydrolysis with acids, but not with alkalies, split the alcohol groups taken up. Splitting with acids also caused resin formation. In agreement with an earlier interpretation of the phenomena, Bailey took this to be an indication of the acetal nature of butanol lignin. The fact that alcohol lignins can not be dissolved with bisulfite was also confirmed (246).

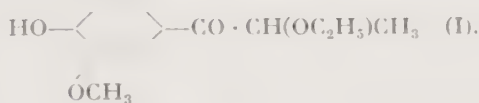
When butanol lignin from Western hemlock was subjected to the action of hydrochloric acid (in butanol-water 1:1, with 1% hydrogen chloride for 3 hours at 160°C) 27.5% of the lignin was converted to low-volatile products (247): 1.9% acetone, 1.6% butyraldehyde, 2.5% methanol, 2.5% allyl alcohol, 4.8% propanol, 11.4% formic acid, and 2.8% β -ethyl- α -methylacrolein. Hydrolysis caused all of the methoxyl (15.2%) in the lignin to be split, but only a small portion of it was recovered as methanol. The major portion is presumably oxidized to formic acid.

The propyl and allyl alcohols, which amount to about one third of the low-volatile substances, probably derive from the propane chain of the lignin. Recently, Bailey (247 a) has isolated a further 15.5% of the butanol lignin, after treatment with hydrochloric acid, in the form of high-volatile substances. Oddly enough these products consisted mainly of resorcinol monomethyl ether (7.5%) and m-cresol (6.7%). A. Bailey and H. M. Brooks (247 b) found 7.8% β -resorcylic acid after electrolytic oxidation of

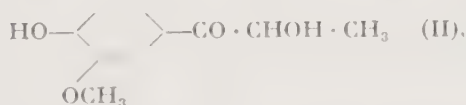
butanol lignin. These results would mean that the lignin preparation used in these experiments should contain *m*-substituted aromatic rings.

L. Friedman and C. R. McCully (248) report that practically quantitative delignification of Western hemlock wood is obtained by digestion with benzyl alcohol containing 3 per cent hydrogen chloride at 105° C during one hour. The benzyl alcohol lignin, isolated by precipitating the extract with ether, contained 9.9% methoxyl and a corresponding preparation from fir 11.1%.

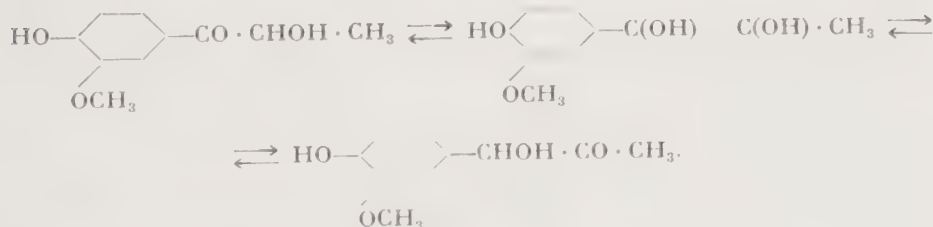
H. Hibbert and his co-workers have met great success in their investigation of the water-soluble products obtained by alcoholysis. When spruce was disintegrated with ethanol-hydrogen chloride solution, and the extract precipitated with water, the aqueous layer contained 1.6% of aldehydes, 1.6% of acids, 3.3% of phenols, and 1.4% of neutral products (based on the weight of the lignin) (249). These products were distillable. The phenol fraction consisted chiefly of α -ethoxypropioguaiacone (I).



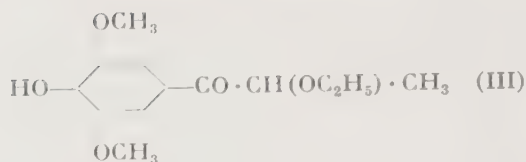
The corresponding alcohol, α -hydroxypropioguaiacone (II).



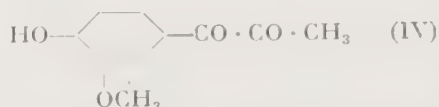
was synthesized, and proved to be a highly reactive substance readily converted to resin by hot, dilute mineral acids. Hibbert considered it likely that this substance as such, or in a condensed form, is identical with native lignin. Compound II could possibly occur in the following tautomeric forms (250):



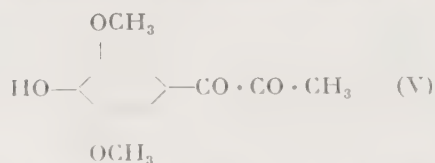
The alcoholysis of maple wood gave a phenolic fraction which consisted of a mixture of equal parts of α -ethoxypropioguaiacone and α -ethoxypropiosyringone (III).



The fraction soluble in bisulfite after alcoholysis of spruce consisted of vanillin and vanilloyl methyl ketone (IV).



and that from maple of syringoyl methyl ketone (V) (251).



The mechanism of alcoholysis was studied by W. B. Hewson, J. L. McCarthy, and H. Hibbert (252). It was found that the yield of water-soluble distillable oil from maple was independent of the state of subdivision of the wood. Treatment of the wood for 9 hours at 180°C with ethanol containing 0.1% HCl caused about 90% of the lignin to go into solution. The delignification proceeded more rapidly and to a greater degree, when aqueous ethanol (1 : 1) was used. This indicates that the concentration of hydrogen ions is an important factor. It probably controls the cleavage of linkages between lignin-lignin or lignin-carbohydrate units or both. With prolonged reaction times a polymerization of the lignin to insoluble products occurs. Similar relations have been found to be valid in ethanolysis with sodium hydroxide as a catalyst. Subsequent treatment of dissolved alcohol lignin for 60 hours with boiling alcohol, containing hydrochloric acid, leads to the formation of about 20% of a product which is difficultly soluble in alcohol.

As Hibbert (253) points out, his interpretation of the course of wood ethanolysis is in general harmony with E. Hägglund's (254) views on the mechanism of sulfite pulping. In both cases the importance of hydrogen and hydroxyl ions for the dissolution of the lignin as well as the necessity of establishing conditions such that the hydrolyzed lignin is actually soluble in the reaction mixture has been recognized.

As for the properties of the amorphous alcohol lignins from maple, H. Hibbert and his co-workers (255) have shown that they can be divided into fractions on the basis of their solubilities in alcohol, pyridine, ether,

and water. Viscosimetric measurements revealed that the different fractions had appreciably different molecular weights (256). It is presumed that this indicates that the lignin fractions have chain-like structures.

J. König (257) has proposed pulping wood with glycerol-sulfuric acid mixtures, for the purpose of obtaining the free cellulose. The delignification with this reagent proceeds with appreciable speed only at high temperatures. König heated the material to 130-140°C for an hour, and most of the lignin appeared to go into solution.

H. Hibbert and J. B. Phillips (258) have studied the action of glycerol monochlorohydrin on sawdust, and established the fact that the glycerol is coupled to the lignin molecule.

Glycol may be advantageously used instead of glycerol as a solvent for lignin. Glycol lignin has been intensively studied by H. Hibbert (259) and his co-workers. They found among other things that a mercurization (based on the work of Freudenberg) indicates that no double bonds are present. B. Rassow and K. Wagner (260) have also used glycol-hydrochloric acid mixtures as a delignifying agent for pine wood and studied the glycol lignin obtained. The varying solubility in chloroform was attributed by these authors to keto and enol forms of the lignin. The keto form, which was insoluble in chloroform, was assigned a higher molecular weight. Conductometric measurements indicated that the glycol lignin from pine wood is a tribasic acid. Poplar wood was also investigated (261). The elementary composition of the glycol lignin from poplar corresponded to the formula $C_{32}H_{29}O_9(CH_3O)_5$. Oxidation of the lignin by oxygen in alkaline solution in the presence of catalysts gave *p*-hydroxybenzoic acid in 6% yield.

The experiments of Hibbert and Phillips have recently been extended by F. Schütz (262). Glycerol monochlorohydrin as well as glycol chlorohydrin, with or without the addition of water, were employed. The lignin is relatively easily dissolved, so that pulps poor in lignin can be obtained. The lignins obtained are mixtures of compounds of various highmolecular polymers. The products contain a few per cent of chlorine, and show a relatively high methoxyl content — 17-18% in the case of spruce. This may be due to the fact that the glycerol or glycol residues which are doubtless incorporated into the molecules give volatile iodides on treatment with hydriodic acid, and thus simulate a high methoxyl content. K. Freudenberg and L. Acker (263) have called attention to this possibility. They also found that the composition of the chlorine-free lignin preparation, 73% C, 5.7% H, 21% CH_3O , 11-14% OH , indicates that the formation of this compound involves a loss of water from one part of the unit, and the opening up of oxygen rings in another part. Also

noteworthy is the finding that glycol chlorohydrin lignins contain 8-14% of sugar. There is here a great resemblance to the cuproxam lignin, which under some circumstances contains 8% of bound hexose. The conclusion was drawn that the lignin is firmly bound to the polysaccharide of the wood. According to Freudenberg, chlorohydrin lignin is not suited as a material for the investigation of lignin structure, since the chemical nature of the original lignin has been so drastically changed (248).

A. Ogait (264) found that spruce lignin dissolved in chloral hydrate plus mineral acid, to give chlorine-containing products. Every third phenylpropane unit was chemically attached to one molecule of chloral.

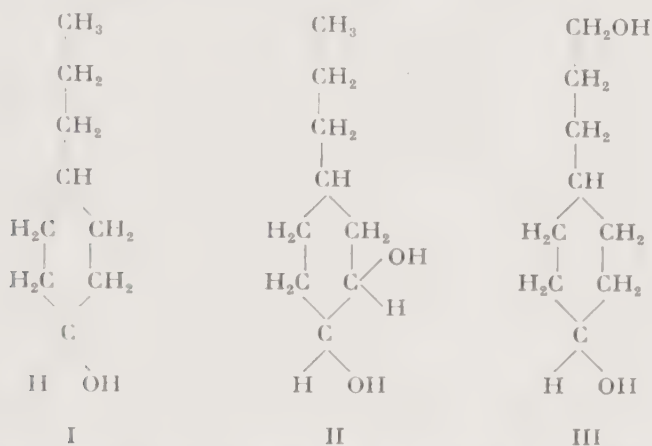
According to a patent by O. Engel and E. Wedekind (265) it is possible to delignify wood completely by means of hot dioxane in the presence of hydrochloric acid. Hopes of basing a new pulping process upon this procedure have not been fulfilled (266). Various experiments have been made upon the lignin which goes into solution. It proved to be soluble in sodium hydroxide, but not in sodium carbonate; this indicates the presence of a free phenolic hydroxyl group. The lignin appeared to react with benzenediazonium salts to give dyestuffs (267). K. Storch (268) emphasizes the fact that dioxane is a particularly interesting solvent for lignin, because it contains no reactive groups. The elementary analysis of beech dioxane lignin agrees best with the formula $C_{18}H_{26}O_7$ for the basic substance; on the assumption that this is correct, two CH_3O and two OH groups were found. The dioxane lignin condenses with phenols, in the ratio of one phenol to one unit with the molecular weight given above.

K. Freudenberg, F. Sohns, and A. Janson (269) have emphasized, however, that isolated lignin (cuproxam lignin) has only a limited solubility in *pure* dioxane.

H. Perrenoud (270) has investigated the state of dioxane lignin in solution, and the size of the particles. The lignin was obtained by extraction of spruce wood with boiling dioxane containing 0.175% of HCl . It was purified by electrodialysis. About two thirds of the lignin in the wood could be extracted. Extraction for 24 hours caused 13% of the wood to be dissolved as dioxane lignin; the product, after purification, had 64.3% C, 4.46% H, 13.2% CH_3O . The particle size was determined by dialysis of the solutions in dioxane and sodium hydroxide; it was about 2,300. The lignin solutions were practically monodisperse. The particle size was approximately doubled by the action of sulfuric acid, or by oxidation.

Pressure *hydrogenation* of methanol lignin in dioxane by E. E. Harris, J. D'Ianni, and H. Adkins (271) gave results of great importance for the elucidation of the structure of lignin.

Aspen wood was used as the raw material. Alcoholysis with methanol containing 3% of HCl extracted about two thirds of the lignin. This methanol lignin was dissolved in dioxane and submitted to pressure hydrogenation at 200-350 atm. in the presence of copper and chromium oxides, and at a temperature of 250-260 C. There resulted, in addition to large quantities of methyl alcohol, 44% of a mixture of 4-propylcyclohexanol (I), 4-propyl-1,2-cyclohexanediol (II), and 3-(4-hydroxycyclohexyl)-1-propanol (III):



These results were confirmed by H. P. Godard, J. L. McCarthy, and H. Hibbert (272), who used maple and spruce woods. They found the same products as Adkins when they hydrogenated sawdust suspended in dioxane with the same copper-chromium catalyst. The very high yields of these products, reported by Godard, McCarthy and Hibbert, however, have later been shown incorrect (272a). H. Hibbert and his co-workers (273) also hydrogenated in the same way the ethanol lignin obtained by alcoholysis of maple wood. Product (III) was then obtained in considerably lower yields; this circumstance has led Hibbert to assume that aspen and maple lignins must have different constitutions.

Hibbert and his co-workers (273) also showed that the propylcyclohexanol found could be obtained in 78% yield by hydrogenation of α -ethoxypropionguaiacone.

The behavior on hydrogenation of various fractions of alcohol lignin was also investigated (273). It was found that the yield of water-soluble and distillable hydrogenation products increased with the increasing solubility of these fractions, and with their increasing ability to depolymerize to simpler substances. The supposition has been expressed that acetal linkages exist between the units of the lignin in the easily soluble fractions whereas the fractions which are difficult to dissolve and to split contain predominantly carbon-carbon linkages between the lignin units (274).

J. F. Saeman and E. E. Harris (275) hydrogenated aspen methanol lignin over Raney nickel at 250°C and 400 atm. pressure for 1 to 5 hours: 24% of the lignin was transformed to volatile substances, which were divided into a water-soluble and a water-insoluble fraction. From the first mentioned ethylene glycol, diethylene glycol and 3-(4-hydroxycyclohexyl)-1-propanol were isolated. The last mentioned fraction contained 4-ethylcyclohexanol, 4-propylcyclohexanol and 2-methoxy-4-ethylcyclohexanol.

b. Phenol Lignins. F. A. Bühler was the first to find that the lignin of wood cells is dissolved by phenol at temperatures of 180-200°C (276). L. Hochfelder (277) attempted to isolate lignin by this method, by distilling off the phenol. The residue was extracted with ether, giving two fractions, of which the ether-insoluble "α-substance" consisted of an amorphous brown powder with a composition corresponding to the formula $C_{22}H_{26}O_6$. No carbonyl or carboxyl groups were present, but there were three phenolic hydroxyls. The "β-substance" could be obtained as a resinous, sirupy mass, after removal of the ether.

The reaction proceeds considerably more rapidly when it is carried out in the presence of small amounts of mineral acids, like 0.03% HCl (278). Good results were obtained in 4-5 hours at 100°C with 0.1% sulfuric acid, or at 80°C with 1% sulfuric acid. The yield of cellulose was about 45% of the weight of the wood. It was established that appreciable quantities of phenol were bound; this was evidently due to a condensation of phenol with the non-cellulose part of the wood. K. G. Jonas (279) also found the same thing. Hydrochloric acid lignin also reacts with phenol at boiling temperatures; according to Jonas, the condensation product distils without decomposition at 230-240°C and 10 mm pressure.

L. Kalb and V. Schoeller (280) as well as R. O. Herzog and A. Hillmer (281) found that phenol homologs and polyfunctional phenols also had a lignin-dissolving action. According to W. Fuchs and L. Bettelheim (282) purified phenol lignin is a light yellow powder which contains no polysaccharides.

I. K. Buckland, F. Brauns and H. Hibbert (283) have made more thorough studies of the properties of the phenol lignin from spruce. They found, in agreement with earlier results, that phenol lignin from spruce wood was not homogeneous. Part was insoluble in ether, and another fraction was soluble in mixtures of ether and dioxane. These two fractions were always obtained in the same ratio, 3 : 1. If the formula for native lignin is taken as $C_{42}H_{32}O_6(CH_3O)_5(OH)_5$, the ether-insoluble fraction had taken up three new phenolic hydroxyl groups by reaction

with the phenol. These new hydroxyl groups could be methylated with diazomethane. Another phenol group coupled in a different way, forming a phenyl ether with one of the hydroxyl groups of the lignin. The formula for the phenol condensation product would thus be $C_{42}H_{32}O_6(CH_3O)_5(OH)_4(OC_6H_5) \cdot 3C_6H_5OH$. Much larger quantities of phenol were found to have entered the portion which was soluble in ether-dioxane mixtures. A fractionation of this type proved to be impossible with the lignin products derived from hydrochloric acid lignin or from Freudenberg lignin.

There are divergent opinions (284) as to the manner in which the phenol groups react with the lignin. E. Wedekind and co-workers (284), for instance, assumed condensation between lignin and the *para*-position of the phenol. A. v. Wacek and H. Däubner-Rettenbacher (284 a) have studied the oxidative degradation of phenol lignin with nitrobenzene in alkaline solution and obtained salicylic acid in addition to vanillin. Similarly, 2,5-cresotic acid and 5-chlorosalicylic acid were obtained from *p*-cresol and *p*-chlorophenol lignins, respectively. These results show clearly that at least part of the phenol condensed with the lignin in the *ortho*-position to the phenolic hydroxyl.

F. E. Brauns and W. H. Lane (285) found that thiophenol reacts with spruce lignin in the presence of hydrogen chloride. Three different condensation products were isolated from the reaction mixture. One of these was insoluble in ether-dioxane; for every 4 C_{10} units it contained 4 thiophenol groups, but only one hydroxyl group which could react with diazomethane. Some of the thiophenol groups were loosely bound; this is not the case with the corresponding phenol compounds. Thiophenol also reacts with the native spruce lignin of Brauns, giving a mixture of products. It is evident from what has been said above that the course of these reactions is extremely unclear.

c. Acetic Acid and Formic Acid Lignins. H. Pauly (286) was the first to dissolve the lignin of wood or straw with boiling 85% acetic or formic acid, to which small amounts of sulfuric or hydrochloric acid had been added. He reported that a practically quantitative separation of the lignin could be effected by cooking for 25-30 hours with 85% acetic acid, containing 0.3% of sulfuric acid. This claim appears dubious, however, inasmuch as the yield of acetic acid lignin from spruce was only 17.5-19%.

These lignins were fractionated by means of their different solubilities in benzene and chloroform or glacial acetic acid, and the properties of the various fractions were investigated. (Pauly, like Powell and Whitaker (287), has designated these lignin products as "lignols.") It was found that the acetic acid lignins from different woods had different properties, as might have been expected. Certain differences in the com-

positions of the lignins from the same wood were also observed; it is doubtful if the lignin products were completely free of acetic acid, for the methoxyl content was exceptionally low, being only about 10.5%. Investigations by O. Routala and J. Sévon (288), and A. Friedrich (289), or more recently, by F. Schütz and W. Knackstedt (290), and K. Freudenberg and E. Plankenhorn (291) have shown that the lignin products have quite normal methoxyl contents (14.5%) when they are free of acetic acid.

The delignification of wood with acetic acid or with other lower fatty acids proceeds extremely slowly when no mineral acids are present. F. Schütz and W. Knackstedt found, for example, that boiling 90% acetic acid without a catalyst dissolved only 3.5% of spruce wood in 24 hours, and 6.0% in 48 hours. Propionic acid behaved in the same way, either in the presence or in the absence of water. On the other hand, Schütz reports that the lignin can be dissolved in 2-3 hours at 110-116°C with chloroacetic acid, even without a catalyst (292). This may be due to a splitting off of part of the chlorine as hydrogen chloride, or to the fact that the hydrogen ion concentration of the acid is sufficient to cause delignification to occur. H. Staudinger (293) indeed found that a 92% solution of the relatively strong formic acid did dissolve a portion of spruce lignin. When too much mineral acid is added, there is a danger that the lignin will condense.

F. Schütz and W. Knackstedt (290) have suggested that magnesium chloride is a particularly suitable catalyst. It is partly hydrolyzed in the 90% acetic acid solution, thus maintaining a moderate concentration of hydrogen ions.

K. Freudenberg and E. Plankenhorn (291), using acetic acid-magnesium chloride mixtures, investigated the properties of the preparation obtained with the following analytical results:

	Analytical Data, % of Lignin		
	Acetic Acid Lignin From Spruce Wood	The Same, Deacetylated Found	Corrected
C.....	64.0	65.6	69.0
H.....	5.7	5.7	5.8
Cl.....	0.6	0.5	0
CH ₃ O.....	13.2	14.6	16.6
CH ₂ O.....	0.5	0.55	0.6
Total OH.....	6.0	12.3	9.0
Phenolic OH.....	—	2.1	3.3
Acetyl, by saponification.....	10.2	0	0
Acetyl, by chromic acid.....	16.3	5.6	6.4
Hexoses.....	11.0	11.0	0
Sulfuric acid lignin.....	80.0	90.8	100
Ash.....	0.4	0.6	0

All of the lignin was removed from the wood by repeated cooking. The lignin proved to be soluble in aqueous alkali, acetone, and pyridine.

but insoluble in water and carbonate solutions. Treatment with alkali removed 10% of acetyl groups; the solubility in alkali, glacial acetic acid, and pyridine was not lost, but the preparation was no longer soluble in dry acetone. Freudenberg points out that the general solubility properties of acetic acid lignins are not due to the acetyl groups which have entered the molecule, but are characteristic of the basic structure of the **acetic acid lignin**.

It is known that hydrochloric acid lignin and cuproxam lignin (cf. p. 276) are insoluble in organic solvents and in alkali. Treatment of hydrochloric acid lignin with acidified alcohols (291), or of cuproxam lignin with acetic acid-magnesium chloride (291) results in the formation of substances which are soluble in alkali and in organic solvents. In the opinion of Freudenberg, there is reason to believe that the solubility is acquired only on treatment of the native lignin with, for example, acetic acid-magnesium chloride. The original lignin is not soluble, the acetyl-free acetic acid lignin being by no means identical with the native lignin. On the other hand, the cuproxam lignin is, according to him, more closely related to the native lignin than are the soluble "organosolv lignins". If it were possible to isolate the lignin in the form in which it occurs in the wood (by enzymatic methods, for example) it would prove to be essentially *insoluble in alkali and in organic solvents*.

Organosolv lignins are distinguished from native lignin, from cuproxam lignin, and from certain acid lignins not only by their solubility, but also by their behavior toward acids, bisulfite, and oxidizing agents.

E. Hägglund (295) has demonstrated that the alcohol lignins can not be dissolved with bisulfite. Freudenberg and Plankenhorn found that acetyl-free acetic acid lignin from spruce is likewise dissolved either not at all or only very incompletely by bisulfite. They also found that this lignin, whether it was derived from wood or from cuproxam lignin, became appreciably soluble in alkali on boiling with dilute hydrochloric acid.

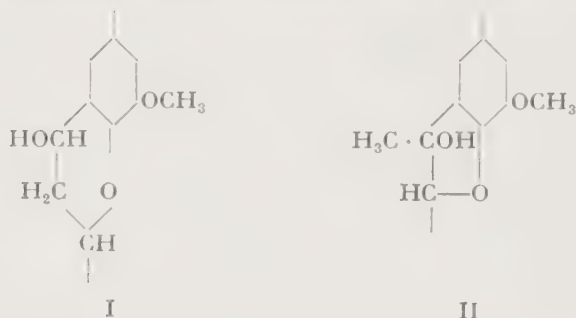
Acetic acid lignin contains appreciably more free phenolic hydroxyl than do cuproxam lignin and hydrochloric acid lignin. Acetic acid lignin has one phenolic hydroxyl group for every three lignin units of molecular weight 178, while hydrochloric acid lignin has one such group for every seven lignin units, and cuproxam lignin has one for every thirteen lignin units (for more recent values cf. p. 286).

Acetic acid lignin from spruce gave 0.5% of formaldehyde on distillation with 28% sulfuric acid (see table, p. 290); cuproxam lignin gave 2.5%. **Organosolv lignins also yield formaldehyde.**

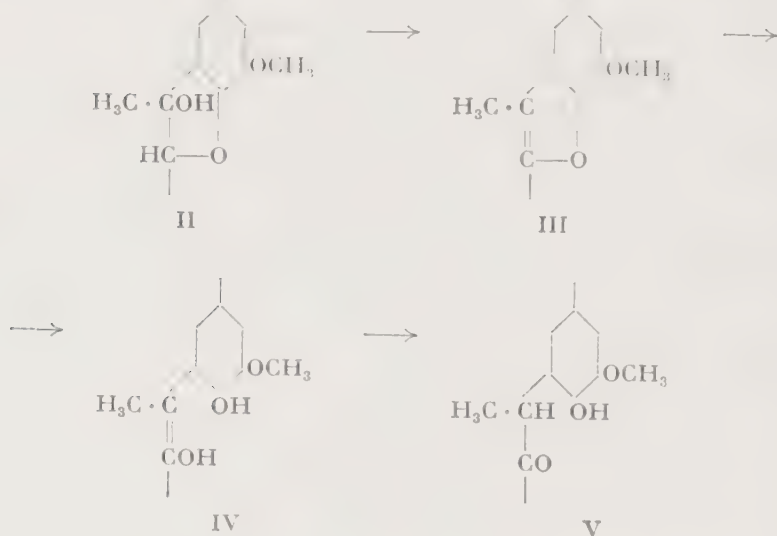
It should also be noted that acetic acid lignin contains considerable quantities of hexosan, as is shown in the above analyses.

Acetic acid lignin and the organosolv lignins differ from cuproxam lignin and from hydrochloric acid lignin in giving much less vanillin when they are oxidized. Some of the lignin units are so altered that they give no vanillin at all.

According to Freudenberg and Plankenhorn (291), the properties discussed above may be explained on the basis of the theory which Freudenberg had previously worked out. He postulated that the spruce lignin molecule contains two different building units, I, and II:



The action of acetic acid causes the following changes in II



According to this scheme the formation of alcohol lignins is to be interpreted as a formation of partly ethers (of I), and partly acetals (of the ketone V). The yields of vanillin can also be explained; it can be formed from II, but not from V.

Concerning these views of Freudenberg, it is, however, necessary to point out that units of formula II probably do not exist in native lignin.

since Hibbert and co-workers (296) have shown that spruce and maple wood as well as maple ethanol lignins do not contain any appreciable amount of C-CH_3 groups.

The fact that acetic acid lignin gives very little formaldehyde on heating with 28% sulfuric acid has caused Freudenberg to abandon his former assumption that spruce lignin contains aromatic methylenedioxy groups (like piperonal, for example). This question will be discussed in more detail in another connection (cf. p. 290). M. J. Hunter, G. F. Wright, and H. Hibbert (297) have studied the problem in detail, and have also come to the conclusion that no methylenedioxy groups are present in lignin. They are of the opinion that the more completely the carbohydrate (or decomposition products) bound to the lignin can be removed, the lower will be the yield of formaldehyde on cooking with acid.

F. E. Brauns and M. A. Buchanan (298) investigated the lignin which they obtained by digesting sprucewood with glacial acetic acid-magnesium chloride mixtures, and found that the hydroxyl content of this acetic acid lignin was the same as that of native spruce lignin. They conclude, in opposition to the views of Freudenberg, that no new hydroxyl groups are formed when spruce lignin is treated with acetic acid.

These authors also believe that they have established the fact that acetic acid treatment causes changes to occur in hydrochloric acid lignin from spruce, consisting in the removal of an aliphatic hydroxyl group from each C_{40} unit of the lignin, and the simultaneous formation of a phenolic or enolic hydroxyl group.

It has already been noted that the alcohol lignins are substances of comparatively low molecular weight (299) when they are carefully prepared, and that H. Hibbert has succeeded in preparing monomeric units, although in small yields. The thermoplastic properties of organosolv lignins may be connected with their low degree of polymerization, in the opinion of Freudenberg. Native lignin is also thermoplastic, but cuproxam and hydrochloric acid lignins have lost this property; the latter must therefore be looked upon as more extensively condensed.

Freudenberg also believes that one can assume that the action of acetic acid makes lignin less suitable for the reaction with bisulfite because it decreases the number of carbinol groups, which are necessary for the sulfonation, or because it so alters the heterocyclic rings which—as Freudenberg believed—are opened by the sulfite (cf., however, p. 314) that the uptake of sulfite is no longer sufficient for a normal sulfonic acid formation.

Formic acid dissolves small quantities of lignin out of wood even in the cold. Part of this lignin proved to be soluble in 66% sulfuric acid.

and in Schweizer's solution. It contained 15% of methoxyl (300). Freudenberg terms the lignin which is soluble in organic solvents *unformed* lignin. In spruce wood it constitutes 4% of the wood; the remaining 24%, which is insoluble, is termed *formed* lignin, because it "displays the morphological features of the tissue." H. Staudinger and E. Dreher (301) have also used formic acid lignin for investigating the molecular weight of lignin.

As mentioned before (cf. p. 196), W. Stumpf and K. Freudenberg (88a) recently found that a large part of the native lignin can be isolated, at room temperature, if wood, which has been pretreated with water, is extracted with dioxane, or tetrahydrofuran, containing 0.35% hydrochloric acid.

G. F. Wright and H. Hibbert (302) isolated formic acid lignin with a view to studying the properties of the hydroxyl groups of spruce lignin, and to determining whether or not carbonyl groups were present. The methoxyl content was low (12-14%). Fractionation of the extract revealed that the easily soluble fraction had higher hydroxyl and lower methoxyl contents than did the difficultly soluble fraction. This might be due to a splitting out of water by condensation.

d. *Thioglycolic Acid Lignin*. B. Holmberg (303, 304) prepared thioglycolic acid derivatives of lignin, usually by heating 10 g. of sawdust for 4 hours with 1 g. of thioglycolic acid in 100 cc. of a 1 N hydrogen chloride solution in absolute alcohol. At least 90% of the lignin was thus converted into lignin thioglycolic acid compounds which were soluble in alcohol and alkali. Even small quantities of water caused noticeable decreases in the yields. The reactivity of alcohol lignin, sulfuric acid lignin, and wood which had been treated with aqueous or alcoholic solutions of HCl was lower. Various softwoods gave lignin thioglycolic acids with the approximate composition $C_{40}H_{40}O_{12} \cdot 3HSCH_2COOH$. It was found that mixtures were actually present, consisting of lignin di- and tetrathioglycolic acids, with the compositions $C_{40}H_{40}O_{12} \cdot 2$ or $4HSCH_2COOH$. As has been remarked, not all the lignin could be dissolved; part of it remained behind in the wood. This lignin had also reacted with the thioglycolic acid. Part of this residue could be extracted with sodium hydroxide. The sensitivity toward alkalis and acids of the lignothioglycolic acid containing the higher amount of sulfur was quite remarkable. At least half of the thioglycolic acid was split off by heating with solutions of mercuric chloride. Reduction of the mercuric to mercurous chloride occurred simultaneously, and vanillin was also formed. True esters are also formed when thioglycolic acid reacts with lignin. When the thioglycolic acid bound as ester is removed, the lignin thioglycolic acid

which remains is by no means completely stable in alkali; one third of the thioglycolic acid is split off by heating with 1N sodium hydroxide. This effect is also noticed when the substance is methylated with dimethyl sulfate in alkaline solution (305). F. E. Brauns and M. A. Buchanan (306) have recently investigated the behavior toward thioglycolic acid of hydrochloric acid lignin and glycol lignin from spruce, as well as from various hardwoods. In general, they confirm the results of Holmberg.

Experiments in which alcohol lignin was treated with thioglycolic acid are also of interest (114). An ethanol lignin with the composition $C_9H_{7.6}O_{2.1}(CH_3O)_{0.9}(C_2H_5O)_{0.5}$, corresponding to one ethoxyl group for every C_{20} residue, gave a preparation with the composition $C_9H_{7.8}O_{1.9}(CH_3O)_{0.9}(SCH_2COOH)_{0.6}$ on heating with thioglycolic acid. According to these results, the ethoxyl groups were replaced by thioglycolic acid residues. It is also noteworthy that continued treatment with thioglycolic acid caused further quantities to be taken up.

Mercapto acids, like thiolactic acid, α -mercaptoisobutyric acid, thiomalic acid, and thiocitramalic acid, react like thioglycolic acid (307). When the resulting compounds were analyzed, and the figures for mercapto groups replaced by equivalent amounts of hydroxyl groups, the following values were obtained for the elementary composition of the lignins:

Lignin from Spruce Wood, Isolated with	% C	% H	% O	% CH_3O
Thioglycolic acid.....	62.34	6.30	31.36	15.31
" "	62.01	5.97	32.02	14.88
Thiolactic acid.....	62.46	6.06	31.48	14.99
α -Mercaptoisobutyric acid....	62.43	6.34	31.20	14.84
" "	61.41	5.93	32.66	14.80
Thiomalic acid.....	62.62	6.36	31.02	15.43
Thiocitramalic acid.....	62.60	6.07	31.33	14.64

The lignin of other woods, and of a large number of other plants, was investigated by the thioglycolic acid method (303, 304). It turned out that the algae, lichens, and fungi gave no lignin compounds with thioglycolic acid. Lignothioglycolic acids with approximately the same composition as those from spruce wood were obtained from leaf stalks of the ferns *Pteris aquilina* and *Dryopteris Filix mas.*, from vascular bundles of the rhizomes of *Dryopteris*, stalks of *Lycopodium annotinum*, leaf stalks of *Cycas revoluta*, and wood of *Ginkgo biloba*. The many angiosperms investigated gave lignothioglycolic acids whose fundamental lignin contained more methoxyl and somewhat less carbon, but more oxygen than did lignin from softwoods. There were, however, exceptions, including *Zostera marina*, which was lignin-free, and *Heracleum sibiricum*, *Bunias orientalis* (Mark), *Potamogeton natans*, *Juncus bufonius*, *Orchis mascula*,

Solanum tuberosum, and *Lathraea squamaria*, which gave both lignin and non-lignin compounds of thioglycolic acid. Holmberg believes that in these latter cases there may be present "semi-formed" lignins which are closely allied to the carbohydrates.

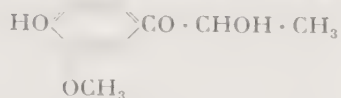
Thiohydracrylic acid has also been tested for its action on spruce wood (308). It turned out that this acid reacted more readily than the others with spruce lignin; the lignin appeared to be completely dissolved. A change in the procedure resulted in the preparation of products which may be derived from a fundamental unit with the formula $C_9H_{9.82}O_{3.95}$ or $C_9H_{10.07}O_{4.01}$.

e. Amines and Hydrazine. Boiling ethanolamine (b.p. 168°C) dissolves the lignin from spruce or beech wood almost completely in 5-6 hours, according to L. E. Wise, F. C. Peterson, and W. M. Harlow (309.) E. Fischer and R. S. Bower (310) investigated the extraction of the lignin from cornstalks with mono-, di-, and triethanolamines, and found that the extractability depended on the alkalinity of the extracting agent. The corresponding amine was chemically bound to the lignin. According to J. D. Reid, E. C. Dryden, and S. I. Aronowsky (311) monoethanolamine causes a partial splitting of methoxyl from the lignin, which then reacts with the amine.

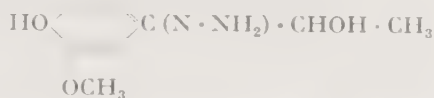
K. Hess and K. E. Heumann (312) broke up rye straw in an oscillating mill, and allowed hydrazine to act upon it at the same time. There resulted a hydrazine compound containing 13% of the straw. The product had 13-14% of methoxyl and 7.1% of nitrogen. The investigators attributed the high nitrogen content to a binding of the base by reactive groups in the lignin, and specifically by *carbonyl* groups. The percentage of nitrogen shows that *one* hydrazine group has entered for every *two* phenylpropane groups. The carbon content of the hydrazine compound was very low, 51.8%, although the lignin of the rye straw itself has 62% of carbon. Hess is of the opinion that this is due to the fact that the lignin isolated with hydrazine has not undergone any secondary self-condensation. The carbonyl groups are probably not liberated by the action of the oscillating mill; it is more likely that the boundary surface between lignin and carbohydrate is laid bare.

These investigations were extended. The action of sodium in alcoholic solution on the methylation product of the hydrazine compound gave nitrogen-free split-products, which were in part volatile; the methyl of an aliphatic methoxyl group was split off. Methylation of the products of sodium splitting gave a propane derivative of veratrole, with a methoxyl in the side chain. This evidently constitutes further proof of the fact that lignin is a derivative of phenylpropane. K. Hess and Yü-Chang-Hwang

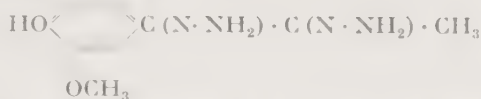
(313) have carried out a model experiment in order to learn more about the hydrazine coupling. They found that α -hydroxypropioguaiacone



with hydrazine gives the expected hydrazone



and that further action of hydrazine at elevated temperatures results in dehydrogenation of the alcohol group with formation of the dihydrazone of the diketone compound, viz.



Strangely enough, the glucose and cellobiose glycosides of α -hydroxypropioguaiacone did not react with hydrazine. On this basis, it is possible to understand the small yields of hydrazine lignin from beech and spruce woods, if one assumes that there is a certain amount of chemical combination between the lignin and the carbohydrate.

3. Alkali Lignin. G. Lange made the first attempt (314) to dissolve lignin with alkali, and then to precipitate it from the alkaline solution. The wood was first submitted to a very extensive purification, which certainly caused appreciable quantities of it to go into solution; this is reflected in the low yields of alkali lignin, amounting to 12% in the case of beech, and 14% for oak. Lange viewed the products as acids, and called them lignin acids. The presence of a number of different substances, rather than a homogeneous material, was indicated by the fact that the lignin could be separated into alcohol-soluble and alcohol-insoluble fractions of different compositions. E. Streeb (315) extended the investigations of Lange to spruce wood, and found that the lignin obtained had a different composition from that which Lange had derived from hardwood. Acidification of the black liquor from a soda pulp factory also yielded lignins with varying contents of carbon and hydrogen.

P. Klason (316) isolated alkali lignin in a similar fashion, and investigated the product, after purifying it by extraction with chloroform. Klason and B. Segerfelt (317) later attempted to isolate and analyze the alkali lignin from a sulfate black liquor in the same way.

B. Holmberg and his co-workers (318) also investigated alkali lignin precipitated with various acids from soda and sulfate black liquors.

H. B. Marshall, F. Brauns, and H. Hibbert (319) found that the alkali lignin from softwoods could be separated into two fractions, an alkali lignin A, which constituted 80% of the total, and was insoluble in mixtures of dioxane and ether, and another fraction (B) which made up 20% of the lignin, and was soluble in dioxane-ether mixtures. The following table shows that there are slight differences in the C, H, and CH₃O contents. The alkali lignins reacted with phenols, and also with acidified methyl alcohol. The elementary compositions of a few alkali lignins from softwoods—mainly spruce—are given in the following table:

Author	Woody Material and Process	Composition in %			Notes
		C	H	CH ₃ O	
Klason	Softwood lignin, precipitated with HCl from soda pulp black liquor, and purified with chloroform.....	65.2	5.4		
Klason and Segerfelt	Softwood lignin, precipitated with CO ₂ from sulfate black liquor, and purified with chloroform.....	63.3	5.2	12.0 to 12.8	
Holmberg and Wintzell	Lignin, precipitated with H ₂ SO ₄ , HCl, CO ₂ , and acetic acid from soda pulp black liquor. Separated into two fractions with alcohol. The alcohol-soluble fraction is α -alkali lignin, the insoluble one is λ -alkali lignin				Empirical formula
	α -alkali lignin	65.7	5.8		C ₄₀ H ₄₂ O ₁₃
	λ -alkali lignin	67.0	6.2		C ₄₀ H ₄₄ O ₁₂
Holmberg and Anderzén	Lignin, precipitated with HCl from sulfate black liquor. .				
	α -alkali lignin	63.4	5.1	10.7	5.6 % Ash, 2.5 % S
	λ -alkali lignin	66.5	5.8	12.3	1.65 % Ash, 1.95 % S
Pringsheim and Fuchs (320)	Lignin, obtained by partial pulping of wood with sodium hydroxide solution, and precipitated from the liquor with HCl.....	62.0	6.3	15.5	The substance contained 5.3 % pentosan
Marshall, Brauns, and Hibbert	Spruce lignin, precipitated from liquors by HCl. Pulping with NaOH by the procedure of M. M. Mehta (321)				
	Alkali lignin A, insoluble in dioxane-ether.....	64.5 to 64.7	5.6 to 5.7	14.9	Ratio of CH ₃ O to phenol OH. 6 : 3
	Alkali lignin B, soluble in dioxane-ether.....	65.0	5.4 to 5.5	14.0 to 14.1	Ratio 9 : 8

These figures may be supplemented with some reports of W. J. Powell and H. Whittaker (322) on the elementary composition of alkali lignin from various woods. The wood was heated under pressure for 6-10 hours at 140-160° C. with 8-12% sodium hydroxide, and the lignin of the black liquor was precipitated with hydrochloric acid, and analyzed. The authors assert that the lignin is only slightly altered under these conditions of pulping—this is, however, quite improbable—and that it is not more highly condensed than the lignin obtained when wood is pulped with sulfurous acid.

Composition, in %, of the Lignin from

	Flax	Larch	Pine	Spruce	Ash	Birch	Poplar
C.....	63.9	63.8	63.4	64.0	63.2	63.2	63.3
H.....	5.8	5.2	5.6	5.5	5.6	5.5	5.8

The lignins obtained were acetylated and methylated, and the derivatives so prepared were analyzed. From the results of these analyses, the conclusion was drawn that all the lignins were derived from a fundamental substance with the formula $C_{41}H_{40}O_{16}$. This substance was termed *lignol*. Powell and Whittaker believed, on the basis of its reactions, that this lignol really consisted of $C_{38}H_{36}O_4(CO)_2CHO(OH)_6$. The lignins of various woods were assumed to differ only in having more or less of the hydroxyls methylated.

The hypothesis that one and the same substance—lignol—is fundamental to all the lignins of wood was supported by the results of treatment of lignin with chlorine or bromine. It was found that such treatment caused most of the methoxyl to be split off. Acetylated lignin was insoluble in cold alkali; this led to the conclusion that carboxyl groups were not present in the lignin molecule, and that the term lignin acid was not appropriate for the lignin obtained by alkali extraction. The acidic properties would, then, be due entirely to the phenol groups.

An alkali lignin from redwood bark has been prepared by F. E. Brauns and H. F. Lewis (323). Its chemical nature has been characterized by methylation with dimethyl sulfate and with diazomethane as well as by acetylation.

F. H. Yorston (324) attempted unsuccessfully to make a fractional precipitation with acetone of the alkali lignin of Powell and Whittaker.

For the molecular weight of alkali lignin values of 1,000-7,000 have been reported (325). Its equivalent weight as a weak acid (phenol) has been determined to be about 200 (326).

F. E. Brauns and I. I. Yirak (326 a) have reported that spruce wood which has been fully methylated can not be delignified by heating with 5% sodium hydroxide solution at 175° C. The wood preparation is recovered

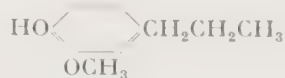
almost quantitatively and apparently unchanged. This result seems, according to these authors, to contradict the assumption that delignification of wood by the soda process is due to a cleavage of oxygen rings with formation of phenolic hydroxyl groups, because there is no reason to believe that methylation of the original OH groups in the lignin prevents this reaction.

B. Holmberg (327) described the alkali lignin which he had isolated as "amorphous powders which very easily form colloidal solutions, behave like high-molecular weight *phenols*, and have, from the preparative point of view, very few agreeable characteristics."

Holmberg found that the alkali lignins had three or four methoxyl groups for each C_{40} complex. Methylation with dimethyl sulfate increased this number to approximately six. The experiments of Powell and Whitaker (322) and of Urban (328) indicate that three more hydroxyl groups per C_{40} group can be methylated.

B. Holmberg and his co-workers found oxalic acid, acetic acid, and protocatechuic acid among the degradation products formed on caustic fusion. Oxidation of alkali lignin with hydrogen peroxide yielded maleic and succinic acids, as well as formic, acetic, and oxalic acids. It is of theoretical interest to note that succinic acid is formed from vanillin under the same conditions.

M. Phillips and M. J. Goss (329) distilled alkali lignin from grain straw with zinc dust, in an atmosphere of hydrogen. The watery distillate contained small amounts of methanol, acetone, and volatile acids. It also contained an oil, which was obtained in 16% yield, and which contained detectable amounts of aromatic substances like guaiacol and pyrocatechol. Even more interesting was the presence of propylguaiacol



Oxidation of the neutral fraction of the oil gave anisic acid



The conclusion was drawn that the straw lignin molecule contains at least two different kinds of aromatic groups.

Phillips and Goss (330) also obtained dihydroeugenol and guaiacol by selenium dehydrogenation of the alkali lignin from corn cobs. The yields were small.

Lignin obtained by carbon dioxide precipitation from soda pulp black liquors [so-called Meadol, from the Mead Corp., Chillicothe, Ohio. Cf. M. Plunguian (331)] was hydrogenated under pressure, with a copper chrom-

ite catalyst, by H. Adkins, R. L. Frank, and E. S. Bloom (332). The starting material contained 65.66% C, 6.37% H, and 23.3% CH_3O . It was soluble in dioxane at room temperature.

The hydrogenation was carried out under a pressure of 200-350 atm.; it lasted 12 hours at 260° C. and 1½ hours at 290° C. The hydrogenation products were practically colorless. Although approximately the same amount of hydrogen was taken up as in the hydrogenation of methyl alcohol lignin, the products were quite different. They consisted chiefly of alcohols and glycols of polycyclic hydrocarbons with 20-70 carbon atoms or more. Cyclohexanol and various alkylcyclohexanols were also formed. When methanol lignin was hydrogenated for comparison, high-molecular products were also formed, but to a much smaller extent than in the case of alkali lignin. The products from alkali lignin contained considerably less oxygen than those derived from methanol lignin; the latter contained 1 oxygen to 6 carbon atoms, while alkali lignin gave products with 1 oxygen to 13.5 carbons.

These facts are regarded by Adkins and his co-workers as evidence for the view that the propylbenzene units of methanol lignin are bound together to form a chain, while the action of alkali on lignin results in cyclization. Pressure hydrogenation over copper-chromium catalysts would then split the bonds between the C_9 units of methanol lignin, while hydrogenation of alkali lignin under the same conditions would affect unsaturated rings, hydroxyl, and methoxyl groups. The rings themselves would be stable.

Results obtained from the pressure hydrogenation of hardwood alkali lignin in a continuous apparatus have been reported by F. E. Harris, J. F. Saeman, and C. B. Bergstrom (332 a). The reaction was carried out at 325° C with copper chromite or at 400° C with stannous iodide as catalysts. In both cases about 70% of the lignin was converted into volatile products. In the first-mentioned experiment these products consisted of water (14%), methanol (8%), phenols (8%), other oxygen-containing compounds (13.3%), unsaturated hydrocarbons (21.8%), saturated hydrocarbons (2%), gases (4%), and high-boiling oils (28%).

Black liquor from pine wood, which contains chiefly a mixture of alkali lignin and saccharinic acids, together with inorganic substances, was hydrogenated under pressure for 5 hours at 340-345° C by W. Lautsch (333). The initial pressure of hydrogen was 140 atm. The neutral products formed amounted to 57.3% of the lignin. A considerable part of the neutral fraction was distillable in a vacuum. When the hydrogenation was carried out at 340-345° C by shaking for 9 hours in an autoclave with Raney nickel at a pressure of 80 atm., products equal to 50.4% of

the acid-precipitable lignin were obtained, of which 33% consisted of phenols, and 37% of distillable materials.

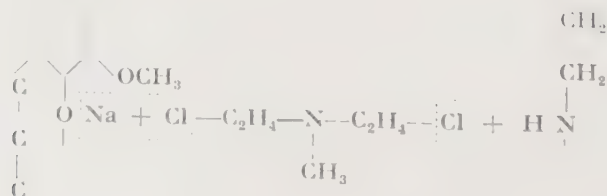
Alkali lignin has often been chosen as the starting material for preparing lignin derivatives. Powell and Whittaker (322) have carried out nitrations with this substance, and obtained preparations with 4.1-4.2% N, corresponding to three nitro groups per C_{40} residue. The lignin is said to be oxidized by nitration, with the probable formation of carboxyl groups. The bromination and subsequent acetylation of wood lignin results in products which are similar to those obtained from flax lignin. Chlorination products—"dodecachlorolignin"—from two wood lignins and from flax lignin also had the same composition.

The Meadol mentioned above has been used by H. F. Lewis, F. E. Brauns, M. A. Buchanan, and E. B. Brookbank (311) for the preparation of a large number of lignin esters. Three to five acid groups are bound to each unit of the molecular weight 860. The higher esters appear to have some practical value, as a lubricant in the preparation of certain plastics, for example.

The preparation of ethers of alkali lignin has been described by F. E. Brauns (335).

Many attempts have been made to utilize lignin from the soda and kraft pulp processes in the manufacture of thermosetting plastics of the phenol-formaldehyde type. It was hoped that these could completely or partly replace the simple phenols, but the success of these attempts appears to have been small (336). Better results have been reported in the manufacture of paper laminates containing about 40% alkali lignin as a binding agent (337). Finally, alkali lignin appears to have a favorable influence on certain mechanical properties of rubber and has therefore been proposed as a rubber filler instead of carbon black (338). According to R. A. V. Raff and G. H. Tomlinson 2nd (339), the rubber-reinforcing properties of alkali lignin are greatly improved, if the lignin is oxidized with air in alkaline solution.

W. Lautsch (340) has described interesting results concerning the preparation of anion exchangers from alkali lignin, for instance by condensation with polyethyleneimine and bis(chloroethyl)methylamine at 50° C. according to the following scheme:



In this way the hydrophilic phenolic hydroxyl groups are blocked and a network-like condensation is achieved. The products obtained are strongly basic and are able to split neutral salts of strong acids by binding the anion and liberating the cation. For instance, NaOH is liberated from NaCl. The ability of the products to split neutral salts can be increased by the introduction of ammonium groups, e.g., by condensation of lignin with the addition product of epichlorohydrine and pyridine, sometimes in the presence of a poly-amine or -imine. The effect of this improvement is illustrated by the following figures:

Anion Exchanger: Condensation Product of	Splitting Capacity for NaCl: Gram-Equivalents NaOH per 1,000 g. Exchanger
Lignin + polyethyleneimine.....	0.015
Pyridine + epichlorohydrin + polyethyleneimine + lignin.....	1.4

A special feature of these lignin exchangers is their ability to bind the anions of high-molecular acids, like, for instance, lignosulfonic acid. This unusual property depends, according to Lautsch, not on the nitrogen concentration of the exchanger molecules but on the swelling properties of the material. Lignin exchangers of favorable composition have been shown to take up lignosulfonic acid in an amount of 150% of their own weight. The absorption capacity for low-molecular acids is controlled by the nitrogen content. It was further shown that it is possible to fractionate lignosulfonic acid, since exchangers rich in lignin absorb the low-sulfonated lignosulfonic acids, while lignin-free polyethyleneimine condensation products adsorb the high-sulfonated lignosulfonic acids.

4. Lignins Prepared by Extraction of Wood with Hydrotropic Solutions. The finding of C. Neuberg (341), that certain salts may increase the solubility of substances in water, has been used by McKee (342) for extracting lignin out of lignified plants. McKee showed that aromatic sulfonates like sodium *m*-xylenesulfonate exerted a strong hydrotropic effect on lignin. The lignin of straw, bagasse, bamboo as well as of poplar and other hardwoods was readily extracted by 30-50 per cent aqueous solutions of aromatic sulfonates at temperatures of about 150°C in 12-14 hours. Some hemicellulose was simultaneously dissolved and pulps with low chlorine numbers were obtained in good yields.

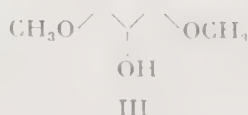
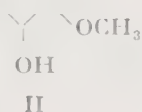
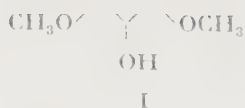
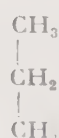
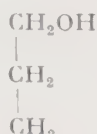
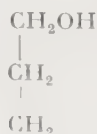
The extracted lignin can be precipitated from the solution by diluting the latter to a lower concentration of the hydrotropically acting salt.

Softwoods can not be delignified to the same degree as hardwoods, which indicates that the lignin in the former is more high-molecular, or less easily split into smaller fragments, or combined with the carbohydrates in a more stable way than the lignin in hardwoods.

During the extraction process the pH of the liquor decreases, probably because of the formation of volatile acids. From unpublished experiments, carried out in the author's institute by S. Rydholm, it appears, however, that these acids are not an essential factor in the delignification. It has been shown, that delignification proceeds to a similar degree, when CaCO_3 is added to the reaction mixtures, to keep the pH nearly neutral.

The lignin preparations obtained by hydrotropic dissolution, are brown powders, which are easily soluble in 0.1 N NaOH, and dioxane, and partly soluble in ethanol. They contain a surprisingly large number of weakly acid (probably phenolic) groups; the equivalent weight has been found to be 260-320 for preparations from aspen, birch and spruce. On heating with calcium bisulfite cooking acid they are, at least partly, dissolved, yielding sulfonic acids which contain 1S for about 20CH_3 .

5. Hydrol Lignin. C. P. Brewer, L. M. Cooke, and H. Hibbert (343) have recently published a new method for the isolation of lignin. They subjected maple wood meal, suspended in aqueous ethanol (1 : 1), to hydrogenation under comparatively mild conditions (over Raney nickel at $165\text{--}170^\circ\text{C}$ for four hours at an initial hydrogen pressure of 3,000 lb. sq. in.). After this treatment 75-80% of the lignin originally present in the wood, could be extracted from the residue with chloroform. After evaporation of the chloroform a clear red-brown viscous oil containing 24-25% OCH_3 remained. This lignin preparation was called "*hydrol lignin*." It contains phenolic hydroxyl and methoxyl groups, but neither carbonyl groups nor ethylenic linkages. The authors assume that this lignin preparation constitutes a practically unchanged, "native" lignin, an assumption, which, however, can hardly be considered proved. The preparation contained petroleumether-soluble substances, which amounted to 10-15% of its weight. From this fraction three monomeric phenolic substances (I, II, III) were isolated.



For the first time phenylpropane derivatives with intact guaiacyl and syringyl groups have thus been obtained by wood hydrogenation. Substance I was isolated in yields of 1.4%, calculated on the basis of the original lignin of the wood, from the petroleum ether-soluble fraction and a further 7.4% of the same substance was found in the ether-soluble fraction of the "hydrol lignin." The yields of substances II and III were 0.84 and 0.83%, respectively. The high yield of the syringyl derivative I compared with the guaiacyl derivative II is in accordance with the theory that the syringyl units are attached to the adjacent unit by $-\text{C}-\text{O}-\text{C}-$ linkages, while at least part of the guaiacyl units are bound by $-\text{C}-\text{C}-$ linkages.

6. Lignins Obtained by the Action of Mineral Acids. In the methods described above for the preparation of lignin, the lignin was brought into solution by various methods, and then isolated from the solution. It is also possible to proceed by the opposite method, saccharifying the carbohydrates, cellulose, and wood polyoses, and thus isolating the lignin which remains undissolved. The hydrolysis can be carried out either with hot, dilute mineral acids, or with cold, concentrated ones.

a. Sulfuric Acid. Strong sulfuric acid has been used as a solvent for carbohydrate by several investigators, like H. Braconnot (344), F. Schulze (345), P. Klason (346), and J. König (347). This reagent sulfonates a part of the lignin, and if the treatment lasts sufficiently long, a part of the lignin is completely destroyed, and goes into solution (348). These statements apply to 73% sulfuric acid. According to P. Klason (349) it is better to use 64% sulfuric acid; a preparation obtained from spruce with this concentration of acid contained 64% C and 5.3% H. The pentosan content was reported as 1.7%. J. König and E. Rump (350) likewise assumed that their lignins contained pentosan, and also that sulfuric acid was retained in spite of careful washing.

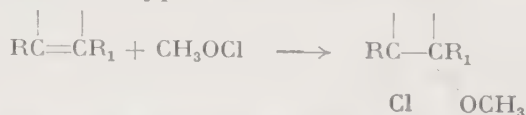
E. Ungar (348) tested sulfuric acid lignins and found that they contained 2.8-6.1% of sulfur, depending on the acid concentration.

P. Klason later recommended that the lignin be treated at the end with hot, dilute hydrochloric acid in order to obtain a product free of sulfur. E. E. Harris and his co-workers (351) have made more careful investigations of sulfuric acid lignin preparations from various woods. They found that the lignin from both hard- and softwoods was soluble to a slight extent in alcohol or acetone. The soluble lignin appeared to have the same composition as the insoluble. Methylation resulted in a methyl-lignin with 32% CH_3O . Chlorination with chlorine gas dissolved in dry carbon tetrachloride yielded chlorolignins with 25-27% of chlorine.

A. G. Norman (352) calls attention to the fact that sugars which may be present when lignin is determined (particularly pentoses) raise the lignin values greatly; he takes this as an indication that the final cooking with dilute acid causes a condensation between the furfural formed, and the lignin.

K. Freudenberg and T. Ploetz (353) assert that the optimum sulfuric acid concentration must be determined in each case. They found, for example, that lignin from spruce and linden is best isolated with 75% sulfuric acid, but that beech lignin is better obtained with 66.5% acid. These concentrations of acid gave products with maximum methoxyl contents. They also confirmed the fact that if the subsequent treatment of the sulfuric acid lignin is omitted, the lignins retain considerable amounts of sulfur (5.2% in the case of spruce lignin, for example.) The yield of sulfuric acid lignin is 1-2% less than the "total lignin" when the optimum concentration of sulfuric acid is used.

E. E. Harris (354) used sulfuric acid lignin from maple wood as a starting material for the investigation of structure. This lignin, with 63.3% C, 5.7% H, and 20.8% CH₃O, contained 6 methoxyl groups, 4 hydroxyls, and 2 double bonds for every C₄₂ unit. Part of the remaining oxygen atoms were possibly present in ether groups, lactones, or furane rings. One of the 4 hydroxyl groups was a secondary one, two were present as acetals, and the fourth was an enol group. The double bonds were determined by treating the lignin, dissolved in methyl alcohol, with chlorine and bromine under such conditions that addition compounds with methyl hypochlorite or hypobromite were formed



b. Hydrochloric Acid. The isolation of lignin with strong hydrochloric acid may well be preferable to that with sulfuric acid, provided that the proper conditions are found (348, 355). The solution of carbohydrate proceeds more rapidly the higher the concentration of hydrochloric acid. For example, if 43% acid is allowed to act at room temperature upon finely divided, pre-extracted sawdust, most of the carbohydrate goes into solution. The residue is a light brown preparation which shows the typical color reactions of lignin (356).

E. Hägglund and his co-workers (357) have established the following facts about the action of very highly concentrated hydrochloric acid upon wood: If the treatment lasts only for a short time, the residue contains carbohydrate. It was also found that considerable quantities of lignin are at first dissolved by concentrated hydrochloric acid, and that

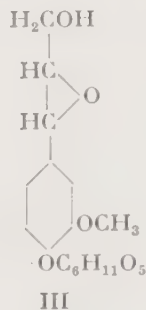
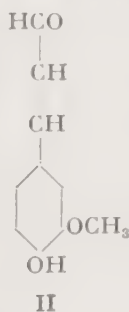
they later precipitate out again. The solutions are at first colored emerald-green; the color may be due to dissolved lignin (cf. p. 191). The solution of the lignin has been confirmed by P. N. Odinzow (358), among others. He found that 26% of the lignin dissolved at -15°C .

Considerable quantities of lignin could be brought into solution by alternate treatment with cold, concentrated hydrochloric acid, and with hot, dilute acid. It can not be said, therefore, that lignin in the state in which it occurs in wood is insoluble in concentrated hydrochloric acid. It is rather so altered by the action of the acid that it *becomes* insoluble.

R. S. Hilpert and E. Littman (359) actually found that when straw was treated with 72% sulfuric acid at -10°C , the whole substance was dissolved. A soda pulp preparation, which contained 6% of lignin according to the usual methods of determination, also dissolved completely in 73% sulfuric acid at $+6^{\circ}\text{C}$.

R. S. Hilpert and H. Hellwege (360) also treated beech wood with hydrochloric acid of d. 1.19, and obtained a product which they regarded as a methylated cellulose anhydride ($2\text{C}_6\text{H}_{10}\text{O}_5 - \text{H}_2\text{O}$) with one methoxyl to two cellulose anhydride residues. Treatment of this substance with 43% hydrochloric acid yielded a product which could be called lignin. Hilpert concluded from this experiment that the lignin is simply formed by the action of acids on carbohydrates and is not originally present in the wood (cf., however, p. 182).

If lignin really did arise by condensation of low-molecular primary substances during the process of isolation, these primary substances could not consist of simple, monomolecular phenols of the phenylpropane series, for experiments of K. Freudenberg, H. Richtzenhain, E. Flickinger, and K. Engler (361) have shown that substances like α -ethoxypropio-guaiacone (I), coniferaldehyde (II), and coniferin oxide (III) do condense



to dark-colored products on treatment with acid, but that the products are soluble in alkali and in organic solvents. It was also impossible to prepare isohemipinic acid from these condensation products, al-

though it is formed from lignin. From these facts Freudenberg concludes that the lignin preparations obtained by the action of acids on wood are not condensation products of these molecules or similar ones, and further, that the native lignin in wood is not formed through changes occurring after the tissue has died, but rather that lignin formation is a physiological process. Freudenberg also assumed that not more than 5-10% of the total lignin of spruce, which is soluble in alkali and cold formic acid (so-called "unformed lignin") could arise by other than physiological processes, and have a low molecular weight; the majority of the lignin of wood must be high-molecular (cf., however, p. 297).

In this connection, the behavior of hydrochloric acid lignin toward bisulfite solutions is interesting. E. Hägglund's investigations (362) have shown that the longer the lignin is acted upon by concentrated hydrochloric acid, the more difficult it becomes to dissolve it with bisulfite solutions. The following table shows that it is nevertheless possible by the action of hydrochloric acid to obtain lignins from wood (see preparation 3) which are almost as easily dissolved as the native lignin. (In this case, but only in this case, does the lignosulfonic acid in the solid and liquid phases show the strong violet fluorescence with ultraviolet light which is characteristic of the lignosulfonic acids prepared directly from wood. The groups responsible for the fluorescence are evidently sensitive to acid.)

No.	Lignin Preparation Method of Preparation	Yield %	Sulfonation with Na bisulfite Solution ($\text{Na}_2\text{O} = 1 \text{ g.},$ $\text{SO}_2 = 5 \text{ g. per } 100 \text{ cc.}$) at 135°C
1	Wood treated for 36 hrs. with 10 parts of 40% hydrochloric acid.....	27.3	53% Dissolved after 20 hrs
2	Wood treated as in 1; the resulting lignin treated for 36 hrs. more with 40% hydrochloric acid.....	27.4	28% Dissolved after 24 hrs 41% Dissolved after 33 hrs
3	Wood treated for $\frac{1}{2}$ hr. with 15 parts of 40% hydrochloric acid.....	28.3	All lignin dissolved after 20 hrs.

It has been asserted that lignin is appreciably more rapidly dissolved in sulfite solution when the pulping is carried out in the presence of cellulose (363). This is not true, however (364).

Proposals have also been made for using mixtures of hydrochloric and sulfuric acids, or of hydrochloric and phosphoric acids, instead of hydrochloric acid alone. H. Urban has tried a hydrochloric-phosphoric acid mixture in Freudenberg's laboratory, and found that the delignification was incomparably slower than with hydrochloric acid alone; indeed it required several days.

The original literature may be consulted for the preparation of hydrochloric acid lignin (365).

The question of the decomposition of wood with strong hydrochloric acid will be taken up again in connection with the saccharification of wood (Chapter IV).

In this connection it should be mentioned that the lignin obtained by treatment of wood with water-free hydrogen chloride according to H. H. Schlubach's method (366) has apparently not yet been further investigated.

Hydrochloric acid lignin has often been used as a *starting material for investigations of lignin*. E. Ungar, who carried out the first investigations in Willstätter's laboratory, found (367) that the product had reducing properties, and contained 15.2% of methoxyl, calculated on the basis of the ash- and chlorine-free material. It was colored by phloroglucinol and aniline hydrochloride, gave furfural on distillation by the Tollens procedure, absorbed 14.5% of HCl, and reacted with fuming nitric acid to form a "nitro compound" containing 6.9% of N, and only a little methoxyl. Much acetic acid was formed at the same time.

E. Hägglund (356) confirmed the results of Ungar, and also found that the hydrochloric acid lignin could be dissolved by the action of alkali. A 5% sodium hydroxide solution dissolved 97.8% of the material in 3 hours at 170°C. Alkali fusion could be shown to yield protocatechuic acid. Chlorine and bromine reacted vigorously with the lignin, but did not give well-defined products. Oxidation with various agents resulted in the formation of acetic acid.

The results of the *dry distillation* may be compared with those obtained later by E. Heuser (368).

Products	% of the Lignin	
	Heuser	Hägglund
Lignin charcoal.....	50.64	45.0
Tar.....	13.00	9.6
Methyl alcohol.....	0.90	0.7
Acetic acid.....	1.09	0.6
Acetone.....	0.19	0.1

The products not listed above were water and gases. The composition of the gases depends upon the manner in which the coking proceeds; this fact is apparent from a comparison of the gas analyses of Heuser and Hägglund. The chief components of the gas were carbon dioxide, carbon monoxide, methane, and hydrogen.

Other investigators have also studied the distillation of lignin. E. Erdmann (369) distilled lignin from pine wood, and obtained 18.1% of tar. More than a third of the tar consisted of creosotes. A characteristic of lignin is the high yield of phenols obtained in comparison with that from cellulose. P. Klason has repeatedly called attention to this fact.

F. Fischer and H. Schrader (370) have carried out extensive investigations of the dry distillation of hydrochloric acid lignin. The yield of "semicoke" was approximately 57%, while that of "primary tar" varied between 9.9 and 14.4%. The major part of the tar consisted of acid substances, chiefly phenols and phenol carboxylic acids. Further investigations in Fischer's laboratory have shown that *vacuum distillation* of hydrochloric acid lignin (at 1-15 mm.) yielded 56.1% of lignin charcoal, 13.3% of tar, and 18.7% of watery distillate. The distillate contained 0.82% of acetic acid (based on the weight of the lignin). By far the largest part of the tar consisted of phenols and carboxylic acids. [Cf. also F. Fischer and H. Tropsch (371)].

The investigations of A. Pictet and M. Gaulis (372) are also important. They distilled technical hydrochloric acid lignin in a vacuum at a maximum temperature of 390° C, and obtained 15% of tar, 21% of aqueous distillate, and 52% of a lignin charcoal containing some ash. The tar was investigated rather carefully. Phenols and acids were extracted from the ether solution with alkali, leaving behind an oil which consisted of high-boiling hydrocarbons, both saturated and unsaturated. The presence of the unsaturated hydrocarbon melene ($C_{30}H_{60}$) could be demonstrated. The acid constituents of the tar were vacuum distilled, and thus fractionated. Pictet and Gaulis found eugenol in the fraction boiling between 210 and 250° C at 10 mm.

B. Rassow and P. Zickmann (373) likewise carried out vacuum distillations and dry distillations of lignin, and isolated 9% of a tar consisting of higher phenols. These investigators considered this to be an absolute proof of the aromatic nature of lignin. Eugenol was shown to be present in the tar.

K. Kürschner (374) subjected lignin preparations to thermal decomposition by heating to about 200° C. He found that vanillin and vanillic acid sublimed, the yield of vanillic acid being 60% of the lignin. The yield was determined by weighing the residue after the heating; this matter has been checked by various investigators, all of whom found considerably smaller amounts of vanillic acid. W. Fuchs (375) estimated the amount at not more than a few per cent of the lignin, and E. Hägglund and T. Rosenqvist (376) also found only small quantities of vanillic acid.

K. Freudenberg and K. Adam (377) subjected acid lignins from both hard- and softwoods to low-temperature carbonization in a stream of hydrogen in the presence of various catalysts, including especially nickel. The following figures on hydrochloric acid lignin from spruce may be quoted:

Distillates from Spruce Lignin

Phenols 35% of the Lignin		Neutral Fraction 6-7% of the Lignin		Acids 0.2-0.3% of the Lignin	
	%		%		%
Phenol.....	5.5	Toluene.....	0.7	Formic acid.....	0.2 to 0.3
<i>p</i> -Ethylphenol.....	1.1	<i>o</i> -Ethylanisole.....	0.5	Acetic acid.....	
Guaiacol.....	3.9	<i>p</i> -Homoveratrole...	2.0	Propionic acid (traces).....	
<i>p</i> -Cresol.....	7.1	Methanol: ethanol...	0.5		
<i>p</i> -Ethylguaiacol....	1.6	Methylcyclopent-			
<i>o</i> -Ethylguaiacol....	0.5	tanol.....	0.2		
Isoeugenol.....	1.3	Cyclohexanediol....	0.5		
Pyrocatechol.....	2.9	Higher boiling frac-			
<i>p</i> -Propylpyrocate-		tions.....	2.0		
chol.....	0.5				
Homopyrocatechol..	1.1				
Higher boiling phe-					
nols (135-180° C					
at 0.03 mm.)....	10.0				

The most important products obtained from spruce lignin were also obtained from beech lignin, though in smaller yields; *p*-cresol was also formed. The total yield of products from spruce lignin, calculated as guaiacol, amounted to 42-60% of the theoretical quantity calculated according to Freudenberg's scheme.

Hydrochloric acid lignin has been subjected to *alkali fusion*, either as such, or after methylation. Protocatechuic acid has been found among the degradation products (356). E. Heuser and A. Winsvold (378) have attempted to determine quantitatively the yields of protocatechuic acid and other materials formed during the fusion. They found that pyrocatechol and oxalic acid were formed, in addition to the protocatechuic acid. The yield depended on whether the fusion was carried out in air or in an atmosphere of hydrogen. The highest yield of pure protocatechuic acid was 12% of the weight of the lignin; only a little pyrocatechol was obtained in this experiment. Another experiment yielded 21.2% of catechol (379).

Several investigators considered this problem again later (380). P. B. Sarkar (381) obtained butyric acid, in addition to the above products, but no vanillic acid (cf. 154); his starting material was jute lignin.

E. Hägglund (382) studied the *pressure heating* of spruce lignin in *alkaline solution*. Technical spruce lignin was almost completely dissolved by treatment for 8 hours at 170° C with 41% of its weight of sodium hydroxide. The lignin solution was then heated under pressure to 350° C., with the addition of varying amounts of NaOH. The yield of tar amounted to as much as 60% of the lignin in some cases; acetic and formic acids, and methyl alcohol (3.5% of the lignin) were also obtained. Practically all of the dissolved lignin reacted.

H. Suida and V. Prey (383) attempted to break down acid lignin into fragments of low molecular weight by heating under pressure with

aqueous or alcoholic alkali. Acid lignins were completely converted to soluble materials with relatively low molecular weights by heating to 300° C with 50 % of slaked lime and alcohol. On the basis of the weight of the lignin, 11 % of neutral oils, 49.5 % of ether-soluble phenols and acids, and 24 % of ether-insoluble phenols and acids were obtained; 60 % of the crude tar was low-molecular, easily volatile, and soluble in ether. The tar obtained in 85 % yield by pressure heating of hydrochloric acid lignin with caustic soda and alcohol at about 300° C was heated for a long time at 430-440° C with decalin and tetralin, and the phenols thus largely hydrogenated to hydroaromatic hydrocarbons and their hydroxy derivatives.

F. Fischer and his co-workers (384) investigated the degradation products formed from lignin by *pressure heating in the presence of oxygen* (pressure oxidation). If the reaction was continued sufficiently long, all the products were water-soluble. The substances formed during pressure oxidation were mainly benzenepolycarboxylic acids, but the yield was low. Doubt has been expressed, however, as to whether benzenepolycarboxylic acids really are formed by oxidation of pure lignin (385).

Other oxidizing agents attack hydrochloric acid lignin easily, usually causing extensive degradation. When concentrated nitric acid was used (386) 20 % of oxalic acid was found among the degradation products.

K. Freudenberg and W. Dürr (387) stated that the course of the action of *nitric acid* on hydrochloric acid lignin is not clear, and that the action ceases only after the formation of products which are not characteristic of the starting material (388).

L. Kalb, F. Plessmann, and H. Lorenz (389) obtained mixtures of nitrophenols and water-soluble degradation products of the lignin. Twenty to thirty per cent of oxalic acid was also obtained. Y. Hachihama and his co-workers (390) had already obtained nitrophenols in 2-3.8 % yield from the waste liquors from nitric acid cooks of bagasse, rice straw, bamboo, and various woods. The nitrophenols isolated contained chiefly 3-nitro-4-hydroxybenzaldehyde, but also 3,5-dinitro-4-hydroxybenzaldehyde, and 3-nitro-4-hydroxybenzoic acid (391).

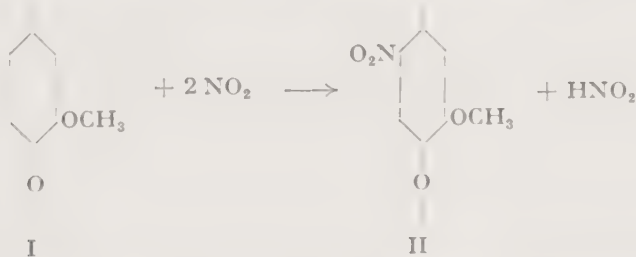
H. Friese and W. Lüdecke (392) succeeded in conducting a nitration in glacial acetic acid or carbon tetrachloride in such a way that nitrogen was taken up only in the form of nitro groups, and not at all in the form of esters. The nitration of lignin caused the methoxyl content to decrease from 15 % to about 4 %; K. Freudenberg (387) had observed the same effect when methyl lignin was treated with nitrogen dioxide. There are considerable differences between the behavior of lignin from which carbohydrate has been removed and that of lignin as it exists in the wood.

The former can not be nitrated without the formation of nitric oxide, for example; this is often accompanied by partial degradation. No evolution of nitric oxide was observed when wood was nitrated.

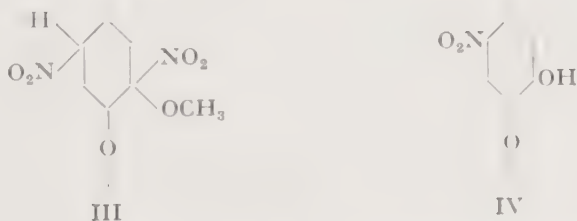
A. Schaarschmidt, P. Nowak, and W. Zetzsche (393) investigated the products of the reaction between hydrochloric acid lignin and nitrogen dioxide. Among other things, addition products were obtained, which decomposed by the Jegorow reaction, splitting off nitrogen and nitrous oxide to form dicarboxylic acids; this behavior indicates the presence of double bonds in the lignin.

K. Freudenberg and W. Dürr (387) are of the opinion that the first action of the nitrogen dioxide is a nitration, and that oxidation is only secondary. If methyl lignin is used as a starting material, the sites of oxidative attack are blocked. Their experiments lead them to the conclusion that the reaction is not due to the presence of double bonds. The nitrolignin can be brominated, for example, taking up 0.7 atoms of bromine for every atom of nitrogen. It is therefore probable that the nitrogen dioxide enters the molecule by substitution.

Up to one third of the methoxyl originally present is lost both on nitration and on bromination. Freudenberg gives an explanation, based on the work of H. Wieland (394). The following reaction first occurs:



Compound II reacts further, with formation of the dinitro-compound III. In this compound the methoxyl is supposed to react to some extent with the neighboring nitro group, splitting out methyl nitrite, ONOCH_3 , with formation of compound IV:



Oxidation with *ozone* yields 1-2% of acetic acid, according to K. Freudenberg and W. Dürr (387). No intermediate products could be isolated.

W. Fuchs and O. Horn (395) have also investigated this reaction; they found that acetylated lignin gives intermediate products which are not volatile. Methyllignin is, surprisingly enough, more easily attacked, according to Freudenberg (396).

F. König (391) oxidized hydrochloric acid lignin with ozone, and found that the reaction products included oxalic acid, and also formic and acetic acids and carbon dioxide. Ozonides were not formed when wood was treated directly with ozone.

E. Hägglund and C. B. Björkman (397) found that *hydrogen peroxide* treatment of hydrochloric acid lignin gave succinic acid among the oxidation products; B. Holmberg had earlier obtained this product from alkali lignin, and from vanillin.

H. Richtzenhain (397 a) oxidized hydrochloric acid lignin with hydrogen peroxide, and isolated 22% of the dissolved lignin in the form of non-volatile acids, of which 8.4% (based on the lignin) were identified; they included veratric acid, isohemipinic acid, lactic acid, and β -hydroxyglutaric acid.

Oxidation of vanillin or of vanillic acid and of lignin gave oxalic, malonic, glycolic, succinic, d,l-malic, and tartronic acids.

F. Freudenberg, W. Belz, and C. Niemann (398) have studied the action of *bromine* on hydrochloric acid lignin. Very large amounts of halogen were consumed when lignin was treated with bromine water or chlorine water; considerable oxidation evidently occurs.

It is possible that the same effects occur here as in the chlorination of alkali lignin, where the uptake of chlorine is accompanied by a splitting off of methoxyl groups. H. Hibbert and his co-workers pointed out that the chlorine will be taken up either in the 5- or 6-position in the guaiacol ring (399). The halogenation induces instability in the methoxyl groupings. These are split off with the formation of quinones and diketo structures which can give rise to acid groups.

If lignin is treated with bromine in hydrobromic acid, the hydrolysis of the bromine is strongly repressed. The lignin then takes up 1 atom of bromine for every methoxyl group. Somewhat more than one atom is also converted to hydrogen bromide. In Freudenberg's opinion, the main reaction is simply a substitution. B. Rassow and P. Zickmann (373) came to the same result. [Cf. also A. W. Walde (400), who treated various lignin preparations with hypobromite and hypiodite.]

When lignin is brominated, methoxyl is split, and approximately one third of the lignin is converted to quinones. Sarkar (385) reports that 8 chlorine atoms per molecule (mol. w. 816) are taken up by hydrochloric acid lignin from jute. Three of these atoms are split off as HCl on treatment with alkali at room temperature. This chlorine may be present

in the side chains since aromatic chlorine is not split off under these conditions.

Hydrochloric acid lignin has also been *reduced*. R. Willstätter and L. Kalb (401) reduced lignins from spruce and beech woods with hydrogen iodide in the presence of red phosphorus at 250° C under pressure. There resulted a mixture of acids and hydrocarbons. Part of the former were soluble in ether, and contained 76.5% of C, and 10.1% of H. Some of the hydrocarbons were insoluble in acetone. They had a composition of 88.66% C, 11.17% H. Those which were soluble in acetone had 87.81% C, and 12.04% H. The average formula would be $\text{CH}_{1.6}$.

The molecular weights of the hydrocarbons ranged between 167 and 812. Willstätter and Kalb thought that they consisted of a mixture of hydrogenated, polycyclic five- and six-membered rings, and that the number of rings increased with increasing molecular weight. Especially interesting is the finding that a similar mixture of acids and hydrocarbons arises when hexites, glucose, xylose, and cellulose are reduced; this would indicate a close connection between lignin and carbohydrates. The following table, giving the results of the hydrogenation of lignins and carbohydrates, shows, however, a considerable quantitative difference.

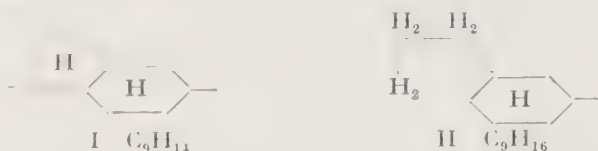
Starting Material	Yield from 100 g. of Starting Material			
	Ether-Insoluble	Liquid	Hydrocarbon Mixture	Total
	Residue		Solid	
	g.	g.	g.	g.
Spruce wood lignin.....	23	16	10	28
Beech wood lignin.....	23	15	17	32
Humus-like substance.....	47	10	10	20
Cotton cellulose.....	9	8	12	20
Glucose.....	3	11	4	17
Xylose.....	14	8	7	16
Mannitol.....	3	12	3	16

Willstätter and Kalb found that the reaction products were not formed by way of hexyl iodide. They assumed that furan derivatives, and possibly also diolefins, appear as reactive intermediates, which tend to polymerize by condensation.

In this connection it may be noted that the experiments of Willstätter and Kalb have served as evidence for W. Schrauth's hypothesis as to the structure of the lignin molecule (402). According to Schrauth, one of the hydrocarbons mentioned was similar to hydrogenated 9,10-benzophenanthrene, as the following figures indicate.

	Boiling Point	d_4^{20}	Mol. Wt.	Empirical Formula
Hydrocarbon obtained from lignin by Willstätter and Kalb.....	150-170° C at 4 mm.	0.9500	243.8	$\text{CH}_{1.72}$
Hydrogenated 9,10-benzophenanthrene, described by Schrauth and Görig..	175-176° C at 17 mm.	0.9425	246.3	$\text{CH}_{1.66}$

K. Freudenberg (403) thinks that an average formula of $(\text{CH}_{1.6})_x$ is compatible with his views of the structure of lignin. On this basis, one would conclude that chains are present in which 4 units with the formula I alternate with one unit with the formula II.



Later experiments of K. Freudenberg and F. Sohns (403) showed that reduction at 150°C yielded a product which had lost the methoxyl groups and the aliphatic hydroxyl, but retained the carbon skeleton.

P. Karrer and B. Bodding-Wiger (404) distilled hydrochloric acid lignin with zinc dust, and obtained an oil, in yields of approximately 17% of the weight of the lignin.

H. E. Fierz-David and M. Hannig (405) were the first to carry out *pressure hydrogenations* of lignin, wood, and cellulose.

These authors first observed that the hydrogen at 300 atm. does not appear to affect the course of the distillation; in the presence of a nickel catalyst, however, the starting materials are almost completely liquified or converted to gas, and a slight hydrogenation occurs simultaneously. The results of the distillation of 500 g. of material are summarized in the following table.

	Cellulose Without Ni g.	With Ni g.	Wood With Ni g.	Lignin With Ni g.
Combustible residue.....	159.0	5.1	19.0	78.0
Total distillate.....	194.0	410.0	401.0	334.0
Aqueous distillate.....	152.0	256.0	272.5	251.0
Tar.....	38.0	168.0	128.5	89.0
Ash, gases, and loss.....	147.0	84.9	81.0	88.0

The composition of the tar is given in the following table. The tar was worked up in the following way: the aqueous distillate was first separated by shaking with ether, and the ether solution was treated successively with bisulfite solution, dilute soda solution, and sodium hydroxide. The "neutral fraction" remained in the ether.

	Cellulose Without Ni g.	With Ni g.	Wood With Ni g.	Lignin With Ni g.
Soluble in bisulfite.....	0.2	8.2	8.5	3.1
First running.....	—	35.5	16.9	7.0
Insoluble in ether.....	5.0	—	9.7	6.2
Acids.....	5.2	9.3	7.7	6.8
Phenols.....	7.6	11.9	30.8	39.0
Neutral fraction.....	15.5	94.1	47.1	21.5
Loss (and water).....	4.5	9.0	8.0	5.4

In this connection, reference may be made to the pressure hydrogenations of lignin in the presence of catalysts, carried out by Harris, Adkins, etc., and also in Freudenberg's laboratory (406).

Y. Hachihama, S. Zyôdai, and M. Umezu (407) described the hydrogenation of hydrochloric acid lignin from *Picea jezoensis*. The methoxyl content of this material was 16.3%, and that of its methylated derivative, which was also hydrogenated, was 30.9%. The hydrogenation was carried out at 230 atm., and at 260-270° C. in the presence of such catalysts as, Ni, Ni oxide, Cu-Cr oxide, ammonium molybdate, and CoS. Dioxane, decalin, methanol, and ethylene glycol were used as solvents. The best results were obtained with Ni oxide in dioxane. One mol. of hydrogen was taken up by 40-44 g. of lignin in 35-55 hours. Methylation destroyed the ability to react with hydrogen. The ether-soluble products, which amounted to 16.7% of the weight of the lignin, contained dihydroeugenol, protocatechuic acid, pyrocatechol, and *p*-hydroxybenzoic acid; the last three substances might have been degradation products of the dihydroeugenol.

E. E. Harris, J. Saeman, and E. C. Sherrard (408) subjected various lignin preparations in aqueous alkali to 6-10 hours' hydrogenation in the presence of Raney nickel, at temperatures of 225-250° C and pressures of 100-175 atm. They reported good yields of various products, including propylcyclohexane and propylcyclohexanol, as well as resins, both soluble and insoluble in alkali.

The pressure hydrogenation in alkaline solution was studied thoroughly by K. Freudenberg and W. Lautsch (409). They found that when hydrochloric acid lignin or cuproxam lignin was treated in the presence of the less active catalysts like copper-nickel-alumina, the products were chiefly phenols, particularly guaiacol, pyrocatechol, and their homologs. About 50% of the lignin was converted into ether-soluble products, about half of which were distillable. Most of these products were phenolic fragments of splitting. Cyclohexanols were the chief products of hydrogenation over the nickel-alumina catalyst of Rupe, which is much more active.

When the temperature was raised to 340-350° C the main products were cyclopentanol and cyclohexanol, whether a catalyst was used or not. As much as 55% of the lignin was recovered as phenolic and neutral products; about 15% of these products consisted of phenols.

W. Lautsch and G. Piazzolo (410) found that the hydrogen consumed in these processes can be derived wholly or in part from substances which will give up hydrogen. In the presence of alcohol, for example, the following reaction occurs:



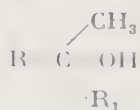
When lignin was heated with 1-2 times its weight of sodium hydroxide and twice its weight of alcohol to about 350° C for 1-2 hours, up to 77% of the lignin was converted into products which were all neutral. Approximately $\frac{2}{3}$ of the products could be distilled at reduced pressure; 30-50% of the distillate consisted of hydrocarbons.

7. Cuproxam Lignin. K. Freudenberg, H. Zocher, and W. Dürr (411) have treated wood alternately with hot, dilute sulfuric acid, and with Schweizer's solution in order to remove the carbohydrate components.

The sawdust is first extracted for 48 hours with a hot mixture of equal parts of benzene and alcohol. Acid constituents are removed by treating twice for 24 hours with cold 5% sodium hydroxide, with frequent shaking, and the residue is washed with much water, with dilute acetic acid, and again with water. Pentosans and other hemicelluloses are partly dissolved by treatment for 3-4 hours with boiling 1% sulfuric acid, and the material is washed and dried. The sawdust is then shaken for 12 hours with Schweizer's solution, separated by centrifugation, and washed with Schweizer's solution and concentrated ammonia. It is then suspended in water, acidified with dilute hydrochloric acid, and washed with water on a Buchner funnel. The treatment with dilute sulfuric acid and Schweizer's solution is repeated two or three times. [Fuller details of the process are given by Freudenberg, et. al. (412)]. The yield of lignin was 16% of the weight of the wood, as compared with 25% obtained by treatment with 66% sulfuric acid.

Freudenberg and his co-workers have made various investigations of this product, obtaining results which agree in general with those obtained with hydrochloric acid lignin. The methoxyl content was 16%, that of C, 66-67%, and of H, 6.1%.

Methylation with dimethyl sulfate and strong alkali gave a product containing 29.2% of methoxyl, although not all of the hydroxyl groups were methylated. According to Freudenberg, the methyl lignin still contains 2.4% of hydroxyl groups which can be acetylated. It is assumed that these are tertiary hydroxyl groups (cf. p. 286), occurring in the grouping

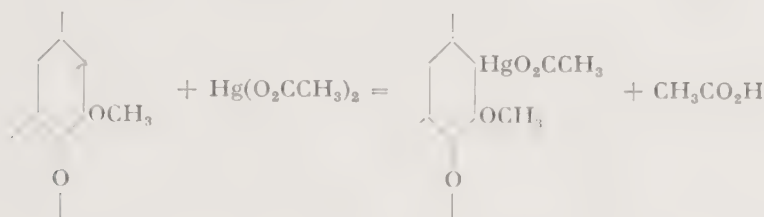


Oxidation of this compound with chromic acid would have to yield acetic acid; this is found actually to be the case. The yield of acetic acid is 6% (calculated 8.8%).

Potash-fusion yielded 10% of protocatechuic acid, which was de-

terminated as pure veratric acid (411). Considerable amounts of protocatechuic acid were also destroyed by the fusion; Freudenberg estimates this loss to about 50%, so that the true yield would be approximately 20% of the weight of the lignin.

The aromatic character of lignin is made clearer by the results which Freudenberg obtained (413) by the action of mercuric acetate according to Dimroth's procedure. A mercuric acetate group replaces a hydrogen atom in the lignin or methyllignin:



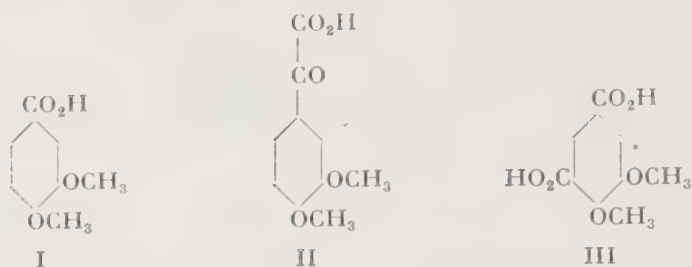
The mercuric acetate is quantitatively displaced by iodine, and the lignin takes up the iodine to form a stable bond, which can not be split to form iodide ion even with 20% potassium hydroxide. The nitrolignin prepared with nitrogen dioxide can also be mercurized in the same way. The general structure of the lignin molecules is not at all affected by the mercury acetate; methyl groups are not split off, either.

Since only small amounts (5.17%) of acetyl are taken up from lead tetraacetate, Freudenberg concluded that cuproxam lignin contains hardly any aliphatic double bonds.

The cuproxam lignin could be sulfonated by bisulfite, although the reaction velocity was low. Approximately two thirds of the lignin was dissolved in 15 hours at 135°C (414). The lignosulfonic acid precipitated from the solution with naphthylamine contained 5.8% S and 10.2% CH₃O. The lignin was therefore completely sulfonated, since it contained 1 atom of sulfur to an equivalent weight of 360, corresponding to about two phenylpropane units.

The cuproxam lignin shows definite lignin reactions; with phloroglucinol it gives a deep red color, and with phenol, a greenish-blue.

It has already been mentioned that cuproxam lignin behaves like hydrochloric acid lignin when it is fused with potash. K. Freudenberg has used another sort of alkaline degradation (301). He heated the lignin with potassium hydroxide for several minutes at only 210° C. The products were methylated and oxidized, and the following substances obtained: 10-11% of veratric acid (I), several per cent of veratroylformic acid (II), and 2-4% of isohemipinic acid (III).



Spruce lignin was used in all the experiments mentioned above; lignin from hardwoods behaves differently in many respects. It contains 21% of methoxyl, instead of 16%; distillation by Tollens' procedure gives only 0.2% of formaldehyde (415). Potash fusion yields gallic acid (416) as well as protocatechuic acid. A. v. Wacek (417) split alkylated beech lignin with sodium alcoholate and found 3,5-dimethoxybenzoic acid. The quantities were too small to enable him to draw any conclusions about the constitution of beech lignin.

Freudenberg later established the fact that cuproxam lignin contains carbohydrates. When the lignin was treated with strong sulfuric acid in the manner employed for the determination of lignin, the polysaccharide was easily removed from the filtrate after the lignin had been separated. The sugar was not present in the form of monoses, glucosidically bound to the lignin, but rather in the form of a few polysaccharide chains (418). Only a few hydroxyls, therefore, were set free when the polysaccharides were removed from the lignin. These hydroxyls were phenolic.

In this connection mention should be made of a preparative procedure employed by Freudenberg. He treated wood as well as cuproxam lignin with solutions of metallic potassium in liquid ammonia, at 20° C. This reagent converted spruce lignin into a derivative which was soluble in methanol and aqueous alkalies, but not in water. Phenolic groups were set free, rendering the lignin soluble in alkali (418). Calculation showed that the treatment of wood with potassium in ammonia released one hydroxyl group for every two lignin units.

N. N. Shorygina and T. Ya. Kefeli (418 a) confirmed the finding of Freudenberg and co-workers (418) that treatment of cuproxam lignin with alkali metal in liquid ammonia results in the liberation of phenolic hydroxyls and a decrease in the molecular size.

8. Periodate Lignin. The ability of periodic acid and its salts to split the —C—C— linkage of glycols and consequently also of sugars and polymeric carbohydrates (419), has opened up a new possibility for isolating the lignin from wood by breaking down the cellulosic and hemicellulosic components. P. F. Ritchie and C. B. Purves (419 a, 419 b) subjected wood

meal to oxidation with aqueous 5 per cent sodium paraperiodate, $\text{Na}_3\text{H}_2\text{IO}_6$, at pH 4 and 20°C, alternately extracting the oxidized carbohydrates with boiling water at a pH near 7. After five or six of these oxidation-extraction cycles "periodate lignin" remained as a golden-brown powder. The product obtained from black spruce analyzed 92-97% Klason lignin and accounted nearly quantitatively for all the latter in the original wood. Periodate lignins from hardwoods contained between 72 and 78.5% of Klason lignin. The periodate treatment did, however, not leave the lignin unaffected; the low carbon contents of 55-61% and, in the case of spruce, a low methoxyl content of 12% revealed that rather considerable oxidation had occurred. The authors believe, however, that probably no other changes than oxidation, especially condensation, have taken place. The preparations were insoluble in neutral solvents. On ethanolysis, pressure hydrogenation, oxidation with nitrobenzene-alkali and on bisulfite digestion, the periodate lignins behave similar to the lignin *in situ*.

D. THE DEGRADATION OF LIGNIN

1. By Alkali. It was early found that caustic fusion of lignin resulted in the formation of protocatechuic acid and of catechol. The yield of protocatechuic acid from spruce lignin could be pushed as high as 10% of the weight of the lignin. Some catechol was formed at the same time. Since approximately half of the protocatechuic acid was destroyed under the conditions of the potassium hydroxide fusion, it may be supposed that the true yield was 20%.

Gallic acid, as well as protocatechuic acid, is formed from beech lignin, and jute and bamboo lignins yield butyric acid also. The maximum yield of butyric acid from jute lignin was no less than 9% of the weight of the lignin (420).

The large quantities of oxalic acid and carbon dioxide formed during alkali fusion are of no value for the determination of the constitution of lignin.

Freudenberg and his co-workers showed (121) that higher yields of aromatic products are obtained when one starts with methylated spruce wood, carries out the degradation with alkali by heating to 165-170°C in the presence of some water, further methylates the mixture of potassium salts formed with dimethyl sulfate, and finally oxidizes the methylated products with permanganate. In this way, 20% of veratric acid, 6-12% of isohemipinic acid, several per cent of dehydrodiveratric acid, and traces of gallic acid trimethyl ether are obtained.

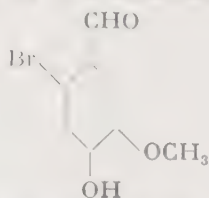
2. By Oxidation. For a long time it was impossible to obtain by direct oxidation any products which threw a light on the problem of the constitution of lignin. The first successful efforts in this direction were the experiments of K. Freudenberg and W. Lautsch (122), who carried out the oxidation with hot nitrobenzene in alkaline solution (optimum temperature 160°C). They obtained as direct products of the oxidation of spruce wood, calculated on the basis of the lignin content of the wood, 27% of vanillin, 1% of phenols of the type of guaiacol, and 10% of phenol carboxylic acids, consisting of vanillic acid and vanillin-5-carboxylic acid. Under similar conditions, R. H. F. Creighton, J. L. McCarthy and H. Hibbert (122 a) obtained 31.8% syringaldehyde and 3.4% vanillin from maple wood, calculated on the lignin content of the wood. W. Lautsch and his co-workers (134) were able to degrade spruce lignin to vanillin by suspending it in potassium hydroxide solution and treating it with oxygen at the boiling temperature in the presence of oxygen carriers, particularly cobaltic hydroxide. The yield was approximately 13% of the weight of the lignin.

I. A. Pearl (123) likewise obtained vanillin, in yields of 9-16% of the weight of the lignin, by oxidation of various lignin preparations with alkaline copper solutions. On oxidation of fermented sulfite waste liquor with silver oxide, Pearl (123) obtained vanillin-5-carboxylic acid in addition to vanillin, vanillic acid, acetoguaiacone, and guaiacol.

Vanillin is obtained by oxidation under pressure even in the absence of catalysts. For example, 9.5% of the lignin in spruce wood is converted to vanillin when sawdust suspended in 10% potassium hydroxide is shaken for 2 hours in an autoclave at 120°C (10 atm. excess pressure).

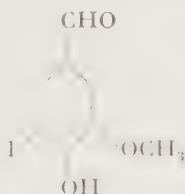
It is supposed that the formation of vanillin is the result of a dehydrogenation, since it occurs under such mild conditions. It is actually found that, in the presence of oxygen, dehydrogenation catalysts, like palladium and platinum, give yields of vanillin up to 11% of the weight of the lignin.

W. Lautsch and G. Piazzolo (125 a) investigated the catalytic oxidation of bromolignin with oxygen in the presence of cobaltic hydroxide. The bromolignin had been prepared by bromination of cuproxam lignin in hydrobromic acid, and contained 1 bromine atom for each lignin unit (mol. wt. 178). An 8% yield of 6-bromovanillin was obtained.



The bromination of vanillin does not yield 6-bromovanillin, but 5-bromovanillin. On the other hand, acetylvanillin is brominated to

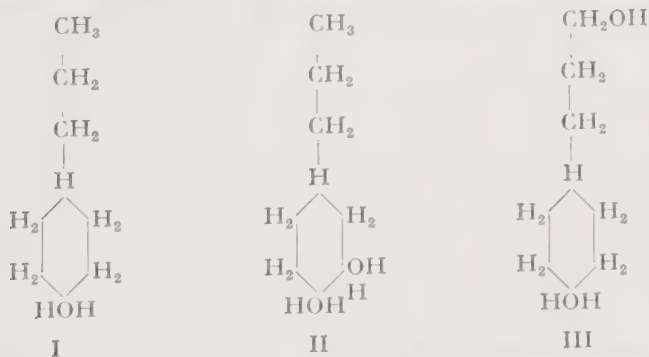
6-bromovanillin. According to Lautsch, this proves that the phenolic hydroxyl group in the lignin is blocked, the lignin units being bound to one another or to the other components of the wood by ether formation. This conclusion is incorrect, however; in the first place, it is not permissible to compare the orienting effects when lignin is brominated with those observed during the bromination of vanillin, and in the second place, creosol, which can be compared with lignin, is brominated in the 6-position [Erdtman (424)], as are homoveratrol and cerulignol (dihydroeugenol) (425). When iodolignin, prepared from the mercuric acetate compound¹ is oxidized in the same way with cobaltic hydroxide, 5-iodovanillin is obtained in approximately 10% yields (425 a).



The conclusion was drawn that only a part of the lignin can have furan or chroman structure.

3. By Hydrogenation. Hydrogen iodide at elevated temperatures reduces lignin to hydrocarbons with properties similar to those of the hydrocarbons obtained from carbohydrates under the same conditions. This method may be too drastic to enable one to draw conclusions about the constitution of lignin.

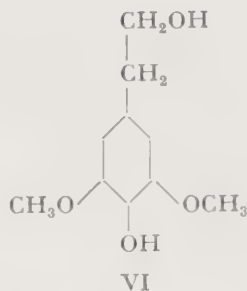
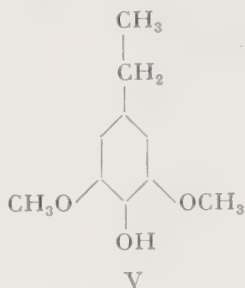
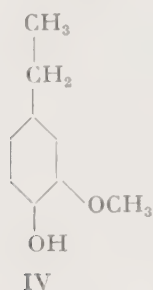
The pressure hydrogenation of lignin in the presence of catalysts, carried out by E. E. Harris, J. D'Ianni, and H. Adkins (427), is of great importance. Methanol lignin from aspen wood was found to yield cyclohexylpropane derivatives like 4-propylcyclohexanol (I), 4-propyl-1,2-cyclohexanediol (II), and 3-(4-hydroxycyclohexyl)-1-propanol (III)



¹The iodolignin was prepared by treatment of the mercuric acetate derivative of methyl lignin with iodine in potassium iodide solution, since the direct iodination of lignin is not possible (426).

That these hydrogenation products are derived from aromatic groups is clearly demonstrated by recent results of H. Hibbert and co-workers. Under milder conditions than those previously used, hydrogenation and hydrogenolysis stops at the aromatic systems.

Thus, in the preparation of "hydrol lignin" (cf. page 262) from maple wood, minor amounts of syringyl- and guaiacyl-propane and -propanol were formed, and under similar conditions, but in the presence of 3% NaOH, the phenylethane derivatives IV-VI



were obtained in yields of 2.2, 15.4, and 6.2% (based on the Klason lignin content of the wood), respectively. According to J. M. Pepper and H. Hibbert (428), the isolation of substance VI "provides some evidence for a carbon-oxygen linkage through the β -carbon atom of the alkyl side chain."

4. By Destructive Distillation. The dry distillation of lignin yields only small amounts of products which are of interest in connection with the determination of structure. The yield of vanillic acid obtained when lignin was sublimed was likewise found to be small.

When lignin is heated in a stream of hydrogen at ordinary pressure, especially in the presence of such catalysts as nickel compounds, large amounts of phenols and neutral substances are formed. Spruce hydrochloric acid lignin, for example, yields 35% of phenols, such as phenol itself, guaiacol, *p*-creosol, catechol, isoeugenol, etc., and 6-7% of neutral bodies, like toluene, *p*-homoveratrol, *o*-ethylanisole, etc. (429).

E. SUMMARY OF CHEMICAL PROPERTIES OF LIGNIN

1. Elementary Composition and Functional Groups. When the data on the elementary composition of the lignin products obtained by various methods are collected from the older literature, rather poor agreement is found. It could nevertheless be concluded that the lignin was by no means a polymeric carbohydrate; this was clearly indicated by the high carbon content, which varied between 63 and 67%, and by the considerable content of methoxyl, which varied, it is true, from 10 to 22%.

As the properties of lignin became better known it became possible to obtain preparations suitable for elementary analysis. Comparison of the results of various analyses still reveal differences which are undoubtedly due to the fact that changes in the molecule are caused by various procedures used for the isolation of the lignin. These changes consist chiefly in condensation reactions, which are associated with the loss of water. In some cases recent data have shown that the lignin preparations were not completely free of carbohydrate.

W. J. Wald, P. F. Ritchie, and C. B. Purves (419 b) have tried to calculate the elementary composition of lignin *in situ* by determining, on the one hand, the percentages of holocellulose and lignin and, on the other hand, the elementary compositions of the original wood and the holocellulose. Since the holocellulose, prepared according to Kurth and Ritter, and the Klason lignin together made up substantially all of the wood, the elementary composition of the original lignin could be calculated. For the lignin of Northern pine and "black spruce," the composition was $C = 67.5\%$ and $H = 6\%$. This constitutes confirmatory evidence for the view that lignin is an aromatic substance and not of hydroaromatic or carbohydrate character.

F. Brauns and H. Hibbert (430) prepared derivatives of lignin by methylation, acetylation, and phenol condensation. Although they started with such varied preparations as glycol lignin, methanol lignin, phenol lignin, hydrochloric acid lignin, and cuproxam lignin, they found on analysis that all the products were derivatives of one and the same basic substance, with the formula $C_{47}H_{52}O_{16}$, or $C_{42}H_{32}O_6(OH)_5(CH_3O)_5$. According to these authors this formula represents the composition of native lignin.

Although the agreement among the analytical values for lignin which are shown in the following table can not be termed excellent it is nevertheless sufficiently good for one to be able to state that lignin possesses a chemical individuality to the same degree as is true of many other natural products. Slight changes in the lignin complex might very easily cause the observed variations.

The elementary composition of lignin shows that the molecule can not possibly be a derivative of saturated aliphatic or alicyclic hydrocarbons. K. Freudenberg, W. Belz, and C. Niemann (431) emphasize the fact that such hydrocarbons must have the composition $(CH_{1.7-2.2})_n$, while the hydrocarbon from which lignin may be considered to be derived has the composition $(CH_{1.4})_n$. Since these authors are of the opinion that reactive double bonds are not present in lignin, the conclusion may be drawn that a benzene ring must be present in the lignin molecule. Heterocyclic rings

containing oxygen, such as furane or pyrane rings, may also be present (432).

Among the functional groups of the lignin, *methoxyl* is the most frequent. This group is bound by ether linkage, rather than as an acetal or ester. The methoxyl is split by hydrogen iodide only at relatively high temperatures; this is also true of aromatic methoxyl groups in general (431).

Lignin Preparation from Spruce	% C	% H	% CH ₃ O	Other Constituents	Author
Cuproxam lignin, values corrected for hexosan (8%)...	65.4	6.4	16.0	HCHO, 2.5%; total OH, 8.2%; phenolic OH, 0.75%	Freudenberg and Plankenhorn (433)
Sulfuric acid lignin, 24 hrs in cold with 72% H ₂ SO ₄	60.4	5.3	14.4		O. A. Müller (434)
Lignin from wheat straw					
48 hrs with 72% H ₂ SO ₄	62.2	6.1	13.7		Ditto
then 48 hrs more with 72% H ₂ SO ₄	64.3	6.1	14.2		
Acetic acid lignin, deacetylated, corrected for hexosan.....	69.0	5.8	16.6	HCHO, 0.6%; total OH, 9.0%; phenolic OH, 3.3%	Freudenberg and Plankenhorn (433)
Cuproxam lignin, treated like acetic acid lignin, saponified; corrected values.....	65.5	6.1	16.2	Total OH, 5.6%	Ditto
Acetic acid lignin					Schütz and Knackstedt (290)
Crude lignin (average values)	65.1	5.7	13.7		
Purified lignin.....	64.5	5.4	13.9		
Formic acid lignin					
Extracted 20 hours.....	63.5	5.3			
" 40 "	63.7	6.7			
" 96 "	65.5	5.4			
" 156 "	66.3	5.3			
Fractions of formic acid lignin obtained with dioxane					(Staudinger and Dreher (178)
Original lignin.....	64.3	5.6	14.2		
First fraction.....	63.2	5.6	13.0		
Second "	62.4	5.4	13.8		
Third "	63.2	5.6	14.2		
Residue, insol. in dioxane..	63.4	5.8	14.2		
Mercapto lignins (mercapto groups replaced by OH)					
Lignin from compounds with					
Thioglycolic acid.....	62.3	6.3	15.3		
" "	62.0	6.0	14.9		
Thiolactic acid.....	62.5	6.1	15.0		
α-Mercaptoisobutyric acid..	62.5	6.3	14.8		
" " ..	61.4	5.9	14.8		
Thiomalic acid.....	62.6	6.4	15.4		
Thiocitramalic acid.....	62.6	6.1	14.6		
average	62.3	6.2	15.0		
Ethanol lignin.....	64.6	6.3			
" " (averages)	63.8	6.2	14.8		
					Holmberg and Runius (231)
					Brauns (435)

Lignin Preparation from Spruce	% C	% H	% CH ₃ O	Other Constituents	Author
Glycol lignin (averages).....	65.0	6.3	15.6		Rassow and Gabriel (436)
Amyl lignin.....	65.9	6.0			Hägglund and Urban (437)
Dioxane lignin.....	64.7	5.6	14.4		Storch (268)
Potassium in ammonia lignin					
Derived from wood.....	65.4	6.9	15.4		Freudenberg,
Derived from cuproxam lig- nin with 8% hexosan....	62.2	6.4	14.8		Lautsch, and Piazolo (438)
Lignosulfonic acids					
Lime precipitation of "α- acid" (hard cook); average of 9 fractions.....	65.9	6.2	15.6	}	Racky (439)
Lime precipitation of "α- acid" (soft cook); average of 16 fractions.....	59.0	6.3	15.3		
Waste liquor from a strong pulp					
Lignosulfonic acid—H ₂ SO ₃ ...	65	6.1	16.7	} Isolated as Ba salts of the acids precipi- table with 4,4'-bis(di- methylami- no)diphenyl- methane }	Erdtman (440)
Lignosulfonic acid—SO ₂	62	6.3	15.9		
Waste liquor from pulp for arti- ficial silk					
Lignosulfonic acid—H ₂ SO ₃ ...	63	6.4	16.3		
Lignosulfonic acid—SO ₂	61	6.6	15.7		
Alkali lignin A.....	64.5	5.6	14.9	}	{ Marshall, Brauns, and Hibbert (441)
Insoluble in dioxane, ether.	64.7	5.8	14.9		
Insoluble in ether.....	64.7	5.7	14.9		
Alkali lignin B.....					
Soluble in dioxane.....	65.0	5.4	14.1	}	
Soluble in ether.....	65.0	5.5	14.0		

Not all of the methoxyl split off from spruce wood is bound to the lignin; part of the methoxyl is bound to the carbohydrate part of the wood, for methoxyl groups were found to be present in wood sugar (442). Quantitative measurements on spruce wood have been made by E. Hägg-
lund and O. Sandelin (443). The methoxyl content was 4.6%, of which 0.56% was bound to carbohydrates. This leaves 4.04% for the lignin, and since the lignin content of the wood was 27.2%, the methoxyl content of spruce lignin should be 14.8%. The values actually found for acid lignins from spruce range from 14 to 15%. The methoxyl content increases to 15-17% only after prolonged hydrolysis with acid.

Free hydroxyl groups are found in the lignin molecule. Almost complete methylation can be achieved with dimethyl sulfate. The hydroxyls which can be methylated are of various kinds; there also occur small amounts of tertiary hydroxyl groups which can not be methylated, but can be acetyl-
ated (444). The methoxyl content of spruce lignin is 21.9% after treat-
ment with diazomethane, while dimethyl sulfate gives a methoxyl
content of as high as 32.4% (445).

Varying quantities of *phenolic hydroxyl groups* are present in various

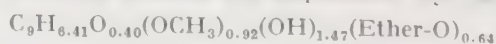
lignin preparations. Freudenberg and his co-workers (146) found no phenolic hydroxyl in extensively condensed acid lignin preparations. Later investigations (147) showed that hydrochloric acid lignin, prepared under mild conditions, contained one phenolic hydroxyl for every 5.0-5.3 lignin units, while cuproxam lignin had only one to every 6.3 lignin units. On the other hand, acetic acid lignin from which the acetyl groups had been removed had one phenolic hydroxyl for every 3.2 lignin units, and liginosulfonic acid was believed to have one for every 3.9 units. The molecular weight of the unit was 178. Peniston and McCarthy (106 c) found a lower value for the phenolic hydroxyls in liginosulfonic acid. According to their conductometric and potentiometric titrations, there is only one free hydroxyl for more than five methoxyl groups.

On the basis of spectrochemical investigations, G. Aulin-Erdtman (106 d) also came to the result that liginosulfonic acids, as well as methanol and acetic acid lignins, contain very little phenolic hydroxyls. It has been found by H. W. Lemon (147 a) that the ultraviolet absorption curves of phenols show an intensification of the absorption and a shift of the maxima toward longer wavelengths when the solutions of the phenols are made alkaline. In the case of lignin preparations, as for instance liginosulfonic acids, the position of the absorption maximum was found to remain practically unchanged on alkalization. On the other hand, Brauns' "native lignin," containing an appreciable amount of phenolic hydroxyls, showed a distinct shift of its absorption maximum in alkaline solution. The same was true for a liginosulfonic acid prepared from "native lignin."

Recently, K. Freudenberg and G. Dietrich (148) have reinvestigated the oxygen distribution in spruce and beech cuproxam lignins, partly with new methods. Their results concerning spruce cuproxam lignin are summarized in the following table (148 a):

<i>Hydroxyl, calc. on C₆-basis:</i>	
Phenolic.....	0.26
Primary.....	0.34
Secondary, not adjacent to the benzene nucleus.....	0.34
Sec. α -phenyl carbinol.....	0.08
Tertiary.....	0.45
Total	1.47
<i>Oxygen (not present in OCH₃ and OH):</i>	
Phenyl ether oxygen.....	0.64
Unknown.....	0.40
Total	1.04

The composition of the spruce cuproxam lignin building unit (184.5) can, according to these values, be expressed by the following formula:



Freudenberg's analyses indicate a content of 1 primary carbinol group for each three C_9 -units, and a very low content of α -phenyl carbinol. It is, however, possible that such carbinol groups may have been present in the original lignin and have been lost during the preparation of the cuproxam lignin. The "unknown" oxygen probably belongs partly to carbonyl groups and partly to tertiary hydroxyl groups.

If, in the formula given above, methoxyl and hydroxyl are replaced by H, and ether and carbonyl oxygen by 2H, one obtains:



From this the composition of the basal hydrocarbon can be calculated. If the "unknown" oxygen is assumed to be present in hydroxyl groups, it can be neglected, but if it is assumed to be present in ether or carbonyl groups it must be replaced by 2H. The resulting basal hydrocarbons will be:



respectively.

A condensed system like



has the formula C_9H_{10} , while phenylpropane is C_9H_{12} .

The fact that hydrochloric acid lignin is able to bind hydrogen chloride in a dissociable form in an amount of 8% of its weight (449) may indicate that 1 ether oxygen to about two units is present as a cyclic ether.

Carboxyl groups are not present in spruce lignin.

Free aldehyde groups have not been demonstrated to be present in several lignin preparations. The reductive power of many lignins may lead to false conclusions, for this may be due to the presence of ortho-dihydroxybenzene groupings. These may arise by the splitting off of methoxyls.

In certain lignin preparations, however, the presence of *carbonyl groups* has been definitely established. F. E. Brauns (61) claimed that the extractable "native lignin" yields a phenylhydrazone, whose elementary composition indicates one carbonyl group for each four methoxyl groups. The analytical data given are, however, insufficient. E. Adler and L. Ellmer (30) reacted "native lignin" in alcoholic solution with hydroxylamine hydrochloride and titrated the HCl liberated during the oxime formation. In this way 1 carbonyl group for each 8 methoxyl groups has been found. Similarly, 1 carbonyl for each 10 methoxyls has been detected in lignosulfonic acids.

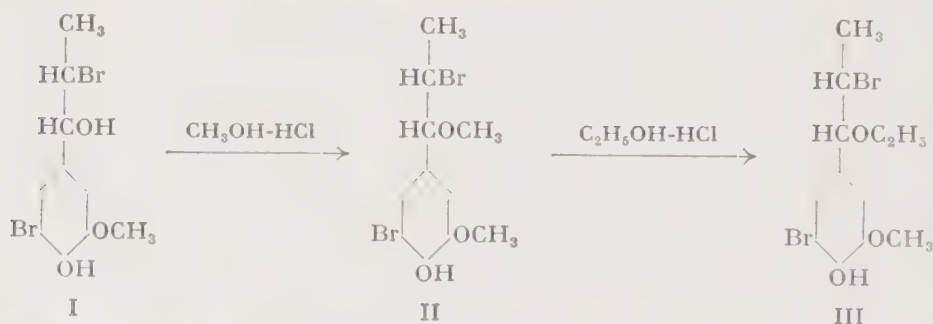
A certain fraction of these carbonyl groups (one for each 40-60 OCH_3)

is present as coniferaldehyde groups (cf. page 190), both in "native lignin" and lignosulfonic acids, and in the original lignin of the wood.

Lignosulfonic acid reacts with aromatic amines to form orange precipitates. These precipitates do not consist exclusively of salts, for the ratio of N to S is greater than one, and not all of the amine can be released by treatment with alkali. Lignosulfonic acids also yield 2,4-dinitrophenylhydrazones [H. Erdtman and co-workers (111), E. Adler (450)]; their nitrogen content corresponds to the presence of one carbonyl group to 7-15 methoxyl groups.

H. Hibbert and G. F. Wright (451) investigated a spruce lignin which was obtained by extraction with formic acid, and found that it contained small amounts of carbonyl groups.

The presence of carbonyl groups in lignin preparations has repeatedly been concluded from the fact that alkoxy groups are introduced on treatment with alcohols in the presence of hydrogen chloride. On the basis of such experiments, F. E. Brauns (61) stated that the so-called "native lignin" contains one carbonyl for each four original methoxyl groups. It should, however, be emphasized that this reaction does not furnish conclusive proof for the presence of carbonyl groups since alcoholic hydroxyls in benzyl alcohol position are also methylated under such conditions. Thus, according to E. Adler and K. J. Björkqvist (unpublished), the carbinol I is readily converted into the ether II, when treated with methanolic hydrogen chloride at room temperature. In addition, it has been shown that the benzyl methyl ether II is readily transesterified to yield the ethyl ether III, on treatment with ethanolic hydrogen chloride at room temperature.



Further model experiments have shown that the ether formation and transesterification, shown above, proceed smoothly even if the activating phenolic hydroxyls have been blocked by methylation. Consequently, the introduction of alkoxy groups into lignin by the action of alcoholic hydrochloric acid may also be due to the presence, in the lignin, of benzyl alcohol or benzyl ether groups (cf. also p. 210).

The question as to whether *double bonds* are present in lignin has been sharply disputed. Bromine in hydrobromic acid solution forms bromolignin and an equivalent amount of hydrogen bromide; this points to a substitution reaction (96). Bromination and chlorination in carbon tetrachloride have given contradictory results; in some cases, the halogen is taken up by addition (452) and in some cases, by substitution (453). E. Hägglund and J. Holmberg (454) investigated the chlorination and bromination of hydrochloric acid lignin in carbon tetrachloride, and found that halogen was taken up without the formation of appreciable amounts of hydrogen halide. In water suspensions, on the other hand, the course of the reaction is quite different, with oxidation, substitution, and addition all occurring.

Double bonds can also be determined with lead tetraacetate (455); the double bonds take up acetate. When this method was applied to cuproxam lignin, it was found that 5.7% of acetyl was taken up (413). This corresponds to one double bond for every eight methoxyls. The same method has been applied to glycol lignin (456), and the resulting compound was found to contain 8.35% of acetyl. (E. Hägglund found 5.9% for hydrochloric acid lignin.) All of these data lead one to no certain conclusions about the presence of ethylenic double bonds.

Both native lignin and isolated lignin preparations take up iodine. According to H. Pauly (457) the iodine enters by addition; neither substitution nor oxidation occurs.

E. E. Harris and L. J. Lofdahl (458) found that sulfuric acid lignin and methanol lignin from maple or spruce reacted with chlorine in methanol solution, giving rise to compounds which contained more methoxyl than the starting material. It was presumed that methyl hypochlorite was formed; this substance is known to add to double bonds. If it is assumed that this reaction proceeds quantitatively one can calculate how many double bonds are present. According to these experiments, an equivalent of lignin of the weight 950 contains two double bonds in the case of maple lignin, and three double bonds in the case of spruce.

Pauly (459) states that maleic anhydride is also added to lignin, which should point to the presence of conjugated double bonds or terminal, single double bonds. In spruce acetic acid lignin, one double bond for each 15 building stones was calculated.

If the treatment of lignin with maleic anhydride is carried out at 170°C, ethylenic linkages in α , β -position to the benzene nucleus may be formed by the elimination of water. The resulting unsaturated lignins then react with maleic anhydride, which results in the formation of water- and alkali-soluble carboxylic acids. Esterification of hydroxyl groups also

occurs. In this way 70% of a lignin, prepared by extraction of poplar wood with hydrotropic solutions (cf. p. 261), was converted into water-soluble derivatives, and poplar wood itself could be practically completely delignified [W. Sandermann (460)].

Treatment of lignin preparations with hydrogen in the presence of catalysts like platinum or palladium sometimes leads to an uptake of hydrogen (461), but in other cases (462) no hydrogen is taken up.

On the basis of all these results, one must conclude that the question as to whether lignin (especially spruce lignin) contains aliphatic double bonds is still undecided.

2. Formation of Formaldehyde—The Absence of Methylenedioxy Groups. E. Hägglund and C. B. Björkman (397), and later E. Hägglund and T. Rosenqvist (463) found that distillation of hydrochloric acid lignin from spruce with hydrochloric acid gave a volatile substance which did not consist either of furfural, methylfurfural, or hydroxymethylfurfural. K. Freudenberg and M. Harder (464) investigated this substance, and found that it was formaldehyde. The formation of formaldehyde was explained by saying that it was derived from a methylenedioxy group. The yield was 0.9-1.2%, but Freudenberg (465) estimated that the content of formaldehyde bound by acetal-like linkages should be around 1.5%, if account was taken of the unavoidable losses. Investigations of E. Hägglund and L. C. Bratt (466) have shown that the yield of formaldehyde depends to a considerable extent on the type of lignin used and on the kind of acid used for the distillation.

With 35% sulfuric acid one obtains yields of formaldehyde varying between 2.0 and 2.3% of the weight of the lignin, depending on the characteristics of the hydrochloric acid lignin (from spruce). P. B. Sarkar (467) obtained 2.6% of formaldehyde when he used 28% sulfuric acid, and Freudenberg and co-workers (468) found with the same reagent 3.0-3.1% formaldehyde from cuproxam lignin, while spruce wood gave 0.9%, which corresponds to the lignin content of the wood.

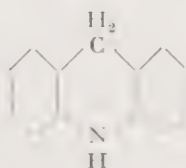
E. Hägglund and H. Urban (469) had found earlier, indeed, that practically no formaldehyde was obtained on distillation with 12% hydrochloric acid of organosolv lignins like amyl alcohol lignin or propyl alcohol lignin, or of acetic acid lignin from spruce. Completely sulfonated lignosulfonic acids, like those present in sulfite pulp, also gave no formaldehyde. On the other hand, lignosulfonic acid obtained from sulfite waste liquor did give formaldehyde on distillation with hydrochloric acid, although in smaller quantities than hydrochloric acid lignin.

From these experiments it may be concluded that the entrance of

alcohol or acetic acid residues into the lignin molecule prevents it from splitting out formaldehyde. It was shown that methylenedioxy compounds like piperonylic acid, do not lose methylene oxide groups on acid distillation; it appeared therefore doubtful whether the formaldehyde really comes from methylenedioxy groups (263).

M. J. Hunter, G. F. Wright, and H. Hibbert (170) found that small amounts of formaldehyde are formed from carbohydrates, and they thought, therefore, that it is not impossible that the formaldehyde arises from carbohydrates or their derivatives which are present in the lignin, and that the yield of formaldehyde decreases as the carbohydrate bound to the lignin is removed. This could not be correct, however, for experiments of E. Hägglund and H. Urban (169) showed that hydrochloric acid lignins which had been completely freed of carbohydrates by hydrolysis with boiling 5% sulfuric acid gave more formaldehyde than the lignin which contained carbohydrate.

Freudenberg and co-workers (168) then found that cinnamyl alcohol gives 2% of formaldehyde on distillation with 28% sulfuric acid and they considered therefore that either methylenedioxy groups in piperonyl residues or side chains might be the source of formaldehyde. The former alternative was supported by the finding (171) that several substances with or without methylenedioxy groups yielded formaldehyde on distillation with acid, but that only those which do contain the methylenedioxy group also yield acridan (as do wood and cuproxam lignin)

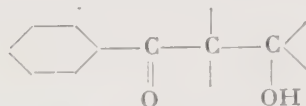
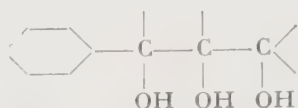


when heated with aniline in the presence of some hydrochloric acid.

Only later, when K. Freudenberg and L. Acker (263) confirmed the fact that organosolv lignins like glycol lignin gave very little formaldehyde, were they inclined to believe that formaldehyde can also be split out of other groups in the lignin molecule. K. Freudenberg and E. Plankenhorn (291) reported that they have found in *p*-hydroxymesityl alcohol and β -hydroxypropioveratrone clear analogies to the group in the lignin which splits off formaldehyde.

In a recent paper, Freudenberg (172) investigated the formation of formaldehyde from 39 substances, on heating with acid, alkali or aniline (formation of acridan). It turned out that substances of the 3-phenyl-1-propanol type yield formaldehyde, especially when the side

chain contains two further hydroxyl groups or a carbonyl group adjacent to the benzene nucleus.



Hydroxybenzyl alcohols and their ethers, too, split off formaldehyde. Some of them also form acridan. From these results Freudenberg concludes that the formaldehyde obtained from lignin can come from phenylpropane units, and that the assumption of methylenedioxy groups is unnecessary.

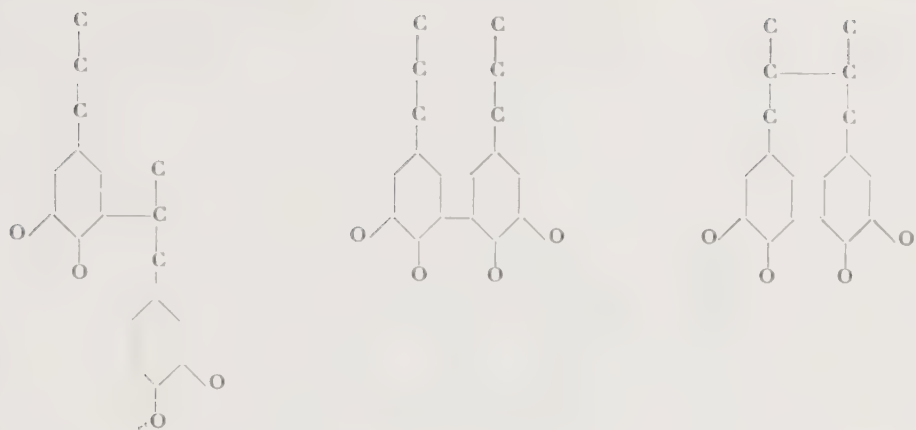
The presence of piperonyl groups in lignin has never been proved, neither in spruce or maple or in sassafras lignin (173, 474), where the existence of such groups might be suspected since the sassafras tree contains piperonal.

F. PHYSICAL PROPERTIES

1. Light Absorption. The ultraviolet absorption of lignin solutions has been studied particularly by R. O. Herzog, A. Hillmer, and their collaborators (175). Comparative spectrochemical investigations of a large number of lignin preparations and lignin derivatives and of various aromatic substances has strongly supported the view that isolated lignin is aromatic in character. Furthermore, a certain group of aromatic compounds has been connected with the structure of isolated spruce lignin. This group has been designated by A. Hillmer (176) as the "third ultraviolet color family"; the simplest member of this family is catechol. Isolated lignin from beech wood, whose spectrochemical properties were first studied by E. Hägglund and F. W. Klingstedt (177), has been assigned to the "fourth ultraviolet family," a group of compounds in which the catechol derivatives are replaced by the corresponding pyrogallols.

R. F. Patterson and H. Hibbert (178) found that the ultraviolet absorption of lignin corresponded satisfactorily with the absorptions of hydroxy derivatives of 1-(4-hydroxy-3-methoxyphenyl)-1-propanone, and of 1-(4-hydroxy-3,5-dimethoxyphenyl)-1-propanone. These authors therefore assumed the presence of a carbonyl group or of a double bond conjugated with an aromatic nucleus; the number of such groups was not definitely established.

G. Aulin-Erdtman (179, 106 d), working in Hägglund's institute, recently studied the spectrochemistry of lignin in comparison with that of a number of model substances with the following general structures:



The lignin used for comparison was liginosulfonic acid from sulfite waste liquors. The shift in the absorption maxima and minima in passing from cerulignol (a simple unit) through dihydro-dehydro-diisoeugenol (two units) to liginosulfonic acid (a macromolecule) furnished a satisfactory explanation of the ultraviolet absorption spectra of the lignin derivatives. These investigations did not furnish any evidence in support of K. Freudenberg's assumption that liginosulfonic acids are formed by splitting of coumarone rings. A comparison between " α " and " β -liginosulfonic acids" was also made; it was found that the β -liginosulfonic acid had, in addition to an absorbing constituent similar to that of the α -liginosulfonic acid, also a methoxyl-free constituent which did not absorb ultraviolet light.

The spectrochemical studies mentioned above support the general idea that *isolated lignin is aromatic in character*. This result is in complete agreement with those obtained by purely chemical means.

Two studies have, however, appeared, in which the absorption is attributed to a **non-aromatic structure**.

A. J. Stamm, J. Semb, and E. E. Harris (108) have expressed the opinion that lignin may be of **alicyclic nature**.

R. E. Glading (481) has attributed the characteristic absorption of lignin to the presence of **flavan and flavanone rings**.

P. W. Lange (482), working in Hägglund's institute, was able to answer the question as to whether *native* lignin had an aromatic character by studying the lignin directly in the cell wall. The absorption of the lignin in the ultraviolet region was studied with an ultraviolet microscope.

Figure 52 represents an ultraviolet microphotograph of a thin cross section of spruce, showing the strongly absorbing, highly lignified compound middle lamellae as well as the weaker absorbing secondary cell walls. The absorption curve had a distinct maximum at 2,800 Å; this made

it certain that native lignin did have an aromatic character. Comparison with various other substances made it quantitatively certain that the aromatic character was essential for the observed absorptions. These investigations were made not in solution, as was the case with all earlier studies, but in the solid phase; in certain cases this led to better agreement



Fig. 52. Ultraviolet microphotograph of a cross section of spruce wood.

between the ultraviolet absorptions of the comparison substances and that of the lignin. Thus, the ultraviolet absorption curve of solid dihydrodehydro-diisoeugenol proved to be very similar to that of the native lignin in wood.

Studies concerning the *infrared* absorption of the "native spruce lignin" of F. E. Brauns have been carried out by E. J. Jones (482 a). In addition to the bands arising from hydroxyl groups and from aromatic and aliphatic C—H groups, a band belonging to a carbonyl group present in a low concentration has been identified. The spectra of sulfuric acid, hydrochloric acid, alkali, periodate, and cuproxam spruce lignins were rather similar to that of "native spruce lignin", whereas the spectrum of "native aspen lignin" differed considerably.

2. Index of Refraction. The fact that lignin has a high index of refraction, 1.61, is important in discussions of the constitution of lignin. Ac-

According to Freudenberg (183), this indicates that lignin definitely belongs to the group of guaiacol, vanillin, and eugenol.

F. Schütz and P. Sarten (184), however, emphasized the fact that the relatively high refractive index of lignin can not be used as an argument for the constitution of the substance, since the refractive indices of cellulose, lignin, and the various layers of the cell walls of wood all lie between 1.53 and 1.62, which is a relatively small interval in view of the uncertainties in the methods of measurement.

3. Molecular Weight. Lignin preparations which are isolated in the form of various derivatives are more or less extensively condensed. This condensation can take place during isolation even in the solid phase, and this may be the reason why it is impossible, for example, to achieve a complete dissolving out of the lignin with acidified alcohol and other organic compounds. This is also true of the dissolving with acid sulfite; here, too, the last traces of the lignin are difficult to dissolve. If the acidity is too great, as is the case when "burnt cook" occurs, so extensive a resinification and condensation of the solid lignosulfonic acid in the wood residue takes place that the dissolving process comes to a halt.

A condensation of this sort can also occur in solution. It is accelerated particularly by mineral acids. The precipitation of lignosulfonic acid from sulfite waste liquors by means of hydrochloric acid is based upon this fact.

Under certain circumstances it is possible to split a condensed lignin into smaller pieces again. When not-too-extensively condensed hydrochloric acid lignin is treated with bisulfite solution, for example, it is dissolved as sulfonic acids of lignins with smaller molecular weights. This solution occurs with swelling; a more or less stiff jelly is first formed, and this gradually changes to a mobile fluid.

Repeated attempts have been made to determine the molecular size of lignin in solution. It has already been mentioned that Klason arrived at values between 900 and 6,000. Alcohol lignins which have been prepared by gentle methods show considerable freezing point depressions, which sometimes indicate a still smaller particle size for the lignin (approximately 400) (185). The results of A. J. Bailey (236) are in agreement with this figure. He found that butyl alcohol lignins from hemlock and aspen showed freezing points in β -naphthol which indicated a molecular weight of 420. E. Wedekind and J. R. Katz (186) report that acetyl phenol lignin is particularly suitable for such investigations. When they used glacial acetic acid as solvent they obtained remarkably small molecular weights (250-270), but when they dissolved the lignin in phenol or naphthalene,

they obtained 1,800. H. Pauly and his co-workers (487) fractionated glacial acetic acid lignin from straw and from various woods, and obtained products which gave molecular weights from 530 to 3,000, by the Rast melting point method.

The native lignin of wood is not soluble in organic solvents unless acid is added. The acid probably causes the lignin to be split from its combination with carbohydrates or with other lignin molecules. This possibly also occurs when hot formic acid is used as solvent without the addition of mineral acids. The lignin products so obtained gave freezing point depressions which, according to Staudinger and Dreher (488), corresponded to molecular weights of about 1,000 [D. L. Loughborough and A. J. Stamm (489) found considerably higher values by measuring the osmotic pressure and the boiling point elevations of lignin solutions. As has been emphasized repeatedly, lignin has a strong tendency toward condensation.]

E. Wedekind and J. R. Katz (486), (cf. also 490), on the basis of spreading experiments, have come to the conclusion that phenol lignin derivatives consist of macromolecules in the form of sheets, while cellulose is extended linearly.

H. Erbring and H. Peter (490 a) investigated the dependence of the viscosity of glycol lignin and glycerol lignin from pine upon the concentration, and concluded that the lignin particles were not linear but approximately spherical in shape.

Finally, B. Holmberg and N. Gralén (491) and N. Gralén (325) have determined the molecular weight of lignin thioglycolic acid compounds by sedimentation and diffusion measurements, using Svedberg's ultracentrifuge (492). The preparations were *polydisperse*; the molecular weights varied between 3,500 and 7,000. A preparation of alkali lignin also had a molecular weight of 7,000. The action of acid or alkali or fresh treatment with thioglycolic acid caused the formation of somewhat monodisperse products of appreciably smaller molecular size. The measurements also seemed to indicate that the molecules of the lignin thioglycolic acid compound had an extended form.

Using the methods of M. af Hällström (492 a), T. Enkvist (492 b) found molecular weights of 1,000-3,000 for some preparations of alkali lignin. By the same method, as well as by the method of Rast, molecular weights of about 1,000 were found for sodium hydrosulfide lignins from spruce (cf. also chapter 6).

W. P. Conner (493) has investigated the molecular weight of lignin by measurements of the dielectric loss. He obtained values of 3,900. Cf. also H. S. Perrenoud (270).

The work of K. Schwabe and co-workers (170) and of D. Pennington and

D. M. Ritter (175) on the molecular size of lignosulfonic acids has already been mentioned (p. 224).

Recently, K. Freudenberg (493 a,b) has reported a value of about 900 for the molecular weight of a methyl lignin isolated from methylated wood by the action of formic acid containing 0.5% of hydrogen chloride, at room temperature. Furthermore, W. Stumpf and K. Freudenberg (88 a) were able to extract a large part of the lignin by treating wood at room temperature with dioxane containing 0.35 % hydrogen chloride. Freudenberg therefore now believes that the bulk of the lignin occurs in the wood in a form similar to the "native lignin" of F. E. Brauns, and has a molecular weight of 800-1,000, corresponding to 4-5 guaiacyl propane units.

Stumpf and Freudenberg assume that the hydrochloric acid, necessary for the extraction of the lignin, resolves hydrogen bonds between the lignin molecules or between lignin and carbohydrate molecules.

However, it would appear possible that the low-molecular lignins obtained by Freudenberg could be the result of an hydrolysis of highly acid-sensitive linkages, such as benzyl ether linkages (cf. p. 210), which hold together in the wood the lignin molecules isolated by Freudenberg.

G. OCCURRENCE AND DISTRIBUTION OF LIGNIN IN WOOD

The question as to whether the lignin is chemically combined with the carbohydrates, or mechanically deposited has been heatedly argued since the very beginnings of the study of wood chemistry.

The idea that the "incrusting" substances are *chemically* bound to the carbohydrate is a very old one. A number of the early investigators like J. Erdmann (494), F. Hoppe-Seyler (495), C. F. Cross (496), H. Schellenberg (497), F. Czapek (498), V. Grafe (26) and P. Klason (499) have expressed themselves as being in favor of this concept.

The *mechanical incrustation theory* is due to A. Payen (500) and has also been supported by P. F. H. Fromberg (501), E. H. v. Baumhauer (502), F. Schulze (503), R. Sachsse (504), J. König (505), and H. Wislicenus (506). C. F. Cross (507) reversed his earlier ideas in favor of this hypothesis.

Let us now consider the evidence upon which these two viewpoints are based.

The incrustation theory is supported first of all by the fact that the treatment of wood with certain chemicals effects what might be termed a spatial separation of the two chief constituents, carbohydrate and lignin.

Upon this fact is based the concept of J. König and E. Rump (508), for example, that a "mechanical binding" of the two constituents of the wood must be assumed. The wood was pulped in various ways and the residues were examined under a microscope. It turned out that the residues obtained by various maceration procedures and consisting of "raw fibers," "cellulose," and "lignin," clearly showed the original structure of the plant membranes.

The so-called raw fibers were obtained by treating wood with a 2% sulfuric acid solution in glycerol. The cellulose—"orthocellulose"—was prepared by treating the wood membrane with 3% hydrogen peroxide in the presence of dilute ammonia, and the lignin, by dissolving the carbohydrates of the wood with 72% sulfuric acid.

Since the residues all had similar structures, the conclusion was drawn that in the cell membranes "there exists an intimate mixture of various substances which have grown together in such a way that one or the other of them can be removed from the whole without destroying the original structure."

K. Freudenberg and his co-workers (509) have further studied the morphology of wood and of lignin. They were long of the opinion that lignification is simply the deposition of lignin substances in a cellular framework which consists essentially of cellulose. This deposition would leave the cellulose structure completely intact. The lignin would be so permeated with cellulose that it would not itself be visible in a stained slide even under the highest magnification. A strong condensation of the lignin with itself would also occur, so that when the cellulose was dissolved out, the remaining lignin would show the form and morphology of the original cell. This process would, however, be accompanied by considerable shrinkage.

According to this point of view, the lignin residue might be compared to a sponge, where the cavities had arisen by the dissolving out of the cellulose. The lignin molecules, which are to be considered as three-dimensional, mesh together to form a large lignin complex, like the mycelium of a fungus, which together with the pectins and wood polyoses, fills up the interstices of the cellulose structure.

Such a concept does not answer the question as to whether chemical combination occurs between the cellulose and the lignin. The argument for chemical combination, which is principally the fact that cellulose can not be dissolved out of wood with the usual solvents, would be vitiated, since the heavy lignin hull around the cellulose would prevent its diffusion; only after the lignin or the wood polyoses had been removed would it be possible to dissolve the cellulose completely (510).

This would explain the results of H. Urban (511), who studied the methylation of wood, lignin, and cellulose. Urban, working in Freudenberg's laboratory, used dimethyl sulfate at low temperature (20°C). The methylcellulose obtained contained 44.5% of methoxyl; it was still fibrous, and dissolved in chloroform among other solvents. The methyl lignin, containing 32% of methoxyl, was on the other hand insoluble in chloroform. Completely methylated wood contained 41% of methoxyl, indicating that both the cellulose and the lignin had been completely methylated. It was not possible, however, to separate the methyl lignin from the methylcellulose by extraction with chloroform. It was found, actually, that both components dissolved *without being separated*.

It should be noted here that E. E. Harris, E. C. Sherrard, and R. L. Mitchell (452) found that part of the hydroxyl groups of the lignin is not accessible to methylating agents until the wood has been hydrolyzed. This would support the view that lignin is chemically linked to the carbohydrates.

On the other hand, P. Karrer and F. Widmer (512) found that when wood is treated with acetyl bromide the reaction products given by lignin and by cellulose can be separated. A. W. Schorger (513) has correctly pointed out that this experiment can not be considered as evidence against a chemical bonding, since acetyl bromide has a strong hydrolyzing action. No reaction occurs in the absence of water and hydrogen bromide (514).

Q. P. Peniston, J. L. McCarthy, and H. Hibbert (515) subjected oak sawdust to acetolysis with acetic anhydride and glacial acetic acid, using sulfuric acid as a catalyst. The reaction product was fractionally dissolved. A fraction soluble in dioxane had, after repeated reprecipitation, a composition practically the same as that of a mixture of lignin, cellulose, and pentosan. This would indicate that a chemical union exists between the lignin and the pentosan, as well as between the lignin and the cellulose.

H. Fries (516) and his co-workers have nitrated sawdust and attempted to separate the components of the nitrated wood by treatment with solvents which dissolve them individually. The attempt was unsuccessful, and the conclusion was drawn that the carbohydrate is chemically bound to the lignin. (According to Fries, it is not possible to determine the lignin content of nitrated wood. He thinks that the nitric acid must attack the molecule at the same point as the sulfuric acid.)

M. Lütke has attempted (517) to explain the chemical properties of wood on the basis of his theory of the structure of fibers. According to this theory the various fiber lamellae and layers are coated with a substance whose identity is unknown. This substance prevents, for example,

the penetration of Schweizer's solution into the native fiber, thus making it impossible to dissolve out the cellulose with this reagent. The coating substance can be rendered permeable by the action of acids or alkalis, or of oxidizing agents. In this case Schweizer's solution penetrates the fiber, to be sure, but the cellulose solution can not get out. This causes the well-known swelling of the fibers which takes place in this medium. If one wishes to dissolve the cellulose it is necessary to break up the woody tissue quite extensively. It is actually found that the amount of cellulose which can be dissolved out increases as the wood is more finely divided. This is shown by the following figures:

Yield of Cellulose Obtained on Extraction of Spruce Wood in Various States of Subdivision

	Wood Meal	Mechanical Pulp	Sawdust
Cellulose and Wood Polyoses	21.16%	10.30%	3.52%

This result was later confirmed by H. Bergström and K. Cederquist (518) and by H. Staudinger (519). [Cf. also the results of J. Levy and E. C. Jahn (520), who confirm the results of Staudinger but who think that the cellulose and lignin are not chemically linked.]

In order to explain the fact that zinc chloride-iodine solutions do not color wood blue (as they do cellulose) but yellow, Lüdtkke assumes that the skin substance is impermeable to this reagent. If the skin is pricked with a needle, or is otherwise injured mechanically, the blue color can be observed with a microscope. According to Lüdtkke, this phenomenon can not be explained on the basis of the assumption that the lignin and the carbohydrate are mixed together, and still less on the basis of the existence of a chemical compound between the two.

Staudinger thinks that the varying solubility of wood cellulose in Schweizer's reagent depending on the subdivision of the wood can be very well explained by the fact that the cellulose molecules are broken into smaller fragments by intensive grinding. He actually succeeded in converting insoluble polystyrenes with a degree of polymerization of more than 1,000 into soluble products with a degree of polymerization of 150-200 by grinding them. Cellulose itself is extensively degraded by treatment in a ball mill. Staudinger thinks that it is very possible that grinding wood causes fragments of the long-chain cellulose molecules to be split off, and that these fragments can then go into solution. But as long as the cellulose is combined with the lignin in the form of three-dimensional macromolecules, it remains insoluble. The great increase in the reactivity and solubility of wood when it is finely divided is also evident from the experiments of K. Hess, K. Jung, and K. E. Heumann

(521). They employed an oscillating mill, which ground the material into particles with dimensions of 1-2 μ . It is not impossible, that such treatment might result in mechanical breaking of the chemical bonds which may exist between cellulose and lignin.

N. Gralén (522) found that when spruce wood was acted upon by ammoniacal copper oxide without previous treatment, only 5-10% of the wood went into solution. Pretreatment of the wood with hot, dilute hydrochloric acid, or with strong alkali made it possible to dissolve two or three times as much material. The dissolved substances consisted of cellulose and wood polyoses. Their sedimentation constants were determined. The values obtained for wood which had not been pretreated were the same as those for wood which had been ground in a ball mill at very low temperatures. The action of acid or alkali resulted in products which were quite different; the wood polyoses were evidently completely hydrolyzed, and the cellulose was also much degraded. From these results Gralén concludes that chemical bonds exist between the lignin and the cellulose. The bonds, were, to be sure, more easily split even than the glucosidic links in polymeric carbohydrates.

The experiments mentioned above may, however, not offer conclusive evidence as to whether or not there is a chemical bond between the carbohydrates and the lignin in wood. More conclusive are the experiments of A. G. Norman and S. G. Shrikhande (523) who pulped silver fir by alternate treatment with sodium sulfite and chlorine. They found that the "hemicellulose" could not be dissolved with sulfite alone. Only when the wood had been pretreated with chlorine could the hemicellulose be dissolved in sodium sulfite. According to Norman it is not to be assumed that the hemicellulose is so changed by the chlorine treatment that it becomes soluble; it is most probable therefore, that the hemicellulose and the lignin are chemically bound together, and that the bond is broken by the action of the chlorine.

T. Lieser and V. Schwind (524) likewise conclude from experiments on the acetolysis of spruce wood that the lignin and cellulose in plant membranes are linked as ethers and esters. The compound is soluble in fuming hydrochloric acid at low temperatures, but is separated into its components at higher temperatures. These conclusions confirm the earlier results of E. Hägglund and his collaborators (525).

H. Friese and his co-workers (526) investigated waste liquors from the sulfite pulping of spruce and beech woods, and found that they contained a lignosulfonic acid-carbohydrate compound, in addition to a high-molecular lignosulfonic acid which could not be split, and a mixture of simple sugars. In the sulfite waste liquor from beech not less than one third of all the lignin was present in the form of the carbohydrate compound.

The investigations of E. Hågglund and his co-workers (p. 216) have shown that the lignosulfonic acid first formed in the solid phase during sulfite cooking goes into solution by hydrolysis. This finding would support the idea that the lignin is chemically combined with the carbohydrate.

Various arguments for the existence of a chemical bond between lignin and carbohydrate have been given by experiments in Freudenberg's laboratory.

The action of pyridine solutions of sulfur trioxide on spruce wood gives rise to a product which can be separated into the following fractions: 1. Salts of polysaccharide sulfuric acid esters. 2. Salts of lignin sulfuric acid esters, free of sugars. Between these two fractions is another which consists of a mixture of salts of polysaccharide sulfuric acid esters and salts of sulfuric acid esters which have been formed from compounds of carbohydrates and lignin (527).

K. Freudenberg, W. Lautsch, and G. Piazzolo (438) investigated the action of metallic potassium, dissolved in ammonia, on spruce wood and on cuproxam lignin from spruce, and found that it caused the hydroxyl content of the lignin soluble in methanol and alkali to increase by a factor of 1.3. They interpret this by assuming that a new hydroxyl group is formed in every third lignin unit, in addition to the secondary hydroxyl group already present in every unit. The new hydroxyl group is phenolic; this explains the solubility in alkali. Since the action is attended by a decrease in the molecular weight, the authors believe that it consists in the opening of ether bridges between the lignin units. The lignin-carbohydrate compound is also split in this manner.

It should again be noted that both acetic acid lignin and alkali lignin retain carbohydrate tenaciously. This carbohydrate is split only with strong sulfuric acid.

On the basis of their recent results concerning the extractability of lignin from wood (cf. p. 297), W. Stumpf and K. Freudenberg (88) now assume that there are no chemical bonds between the extractable parts of the lignin and the other wood constituents. The presence of hydrogen bonds is discussed by these authors.

The question of whether there is a chemical combination between lignin and carbohydrates (in spruce wood) and the various structural possibilities for such a combination have also been discussed by F. E. Brauns and I. I. Yirak (326 a). They prepared fully methylated wood (final OCH_3 content 38.5%) and subjected this to methanolysis and to phenolysis. The properties of the methanol and phenol lignins obtained then might show, whether they contain hydroxyl or carbonyl groups

which had been covered in the wood and liberated during the isolation. The results were, however, not decisive in this respect.

The theory of chemical combination has been supported by the experiments of W. H. Peterson and S. Snieszko (528). They found that the wood pulp obtained by various methods is split to varying extents by fermentation with thermophilic bacteria. These experiments were confirmed and extended by F. R. Olson, W. H. Peterson, and E. C. Sherrard (529), who also found that the bacteria do not attack mechanical pulp which has been extracted, or ground in a ball mill. After the lignin had been removed, the residue (holocellulose) was easily attacked. Good fermentation is obtained only when the lignin content is less than 1%. The authors conclude that the lignin must be chemically rather than mechanically bound to the carbohydrate.

Extensive experimentation on the enzymatic degradation of woods and the constituents of wood has been carried out in Freudenberg's laboratory by T. Ploetz (530). He found that the trunk wood of linden was very resistant to the enzymes of the common snail (*Helix pomatia*), while spruce and beech woods which had been freed from lignin by the chlorine dioxide treatment of E. Schmidt gave holocellulose which was easily attacked. This led to the conclusion either that most of the carbohydrate in the wood was so incrustated by lignin that the enzyme could not get to it, or else that the carbohydrates were chemically combined with the lignin, and that the enzyme was not able to break the bond. To clear up this point, the enzymatic degradation (with snail enzymes) of a fraction of linden wood soluble in ethylenediamine-copper oxide was investigated. It was found that this fraction was at first easily degraded, but that when the ratio of carbohydrate to lignin in the residue had decreased to about 1:1, the degradation became quite slow. Hence one may speak of a "lignin-carbohydrate complex." In the wood itself there exists a carbohydrate-lignin complex with the ratio 3:1, which is resistant to snail enzymes. The intensive action of ethylenediamine-copper solutions so alters this complex that an enzymatic degradation to a complex with the ratio 1:1 is possible.

Investigations of the fermentative degradation of wood and wood pulps with thermophilic cellulose bacteria have led A. I. Virtanen, O. Koistinen, and V. Kiuru (531) to different conclusions. They investigated sulfite pulps with various lignin contents. When the lignin content was 24.4%, 35% of the cellulose could be split by fermentation, and when the lignin content was 18.5%, 80% of the cellulose could be split.

It should nevertheless be emphasized that when the lignin content is 24.4%, approximately one third of the spruce lignin has gone into solu-

tion, and the yield of pulp is about 75%. When the lignin content has dropped to 18.5%, approximately half of the lignin has been dissolved out. Part of the cellulose and the wood polyoses are certainly laid open to the fermenting action of cellulose bacteria by the sulfite process. The fact that about 20% of the cellulose (10% of the weight of the wood) can be fermented directly in the finest birch sawdust is not particularly significant.

A further study of the fermentation of finely divided meal from birch and aspen woods showed that the cellulose and pentosan are quite extensively fermented—up to 80% in the most favorable case. The authors think that it is therefore natural to assume that no chemical bonds exist between the lignin and the cellulose, but do not conclude that this is necessarily the case, since it is quite possible that the cellulose chains are broken by the grinding, and that the cellulose fragments thus split off serve as substrate for the bacteria.

In a recent communication, however, Virtanen (531 a) expressed the opinion that results obtained with thermophilic cellulose bacteria support the assumption that part of the cellulose in the wood is bound to the lignin, while another part is free.

This question is further complicated by the fact that the lignin can also be enzymatically degraded to a certain extent.

This has also been shown by O. Fernández and B. Rogueiro (532), who found that elm wood that had been attacked by an unidentified mold contained 50 per cent lignin but only 2.6 per cent methoxyl.

As far as the *distribution of the lignin* in the wood is concerned, the following facts may be mentioned:

G. J. Ritter (533) treated thin shavings of wood with 72% sulfuric acid to remove the carbohydrates. He concluded that by far the larger part of the lignin was deposited in the middle lamella.

Quantitative measurements of the ultraviolet absorption of thin spruce wood slices, embedded in glycerol were carried out by P. Lange (182) (cf. page 294). They show clearly that the lignin concentration is highest in the compound middle lamella, and that it decreases continuously throughout the cell wall in the direction from the middle lamella towards the lumen.

By measuring the dichroism of lignin in ultraviolet light, Lange finds further, that the native lignin in the middle lamella as well as in the cell wall shows a self-dichroism, which means that it must be orientated or deposited in a preferred direction, to some extent, at least. This fact seems also to support the existence of some type of bond between the lignin and other components of the fiber. During sulfite cooking, the dichroism continually decreases.

K. Freudenberg (534) tried to separate the wood polyoses and the cellulose from the lignin by cooking spruce shavings with 1% sulfuric acid, and then extracting them with Schweizer's solution. These operations were repeated two or three times. Three fourths of the wood was dissolved by these procedures but M. Staudinger (535) nevertheless asserts that the lignin preparations thus obtained still contain some cellulose. The treatment caused much shrinkage of the wood. The very thin middle lamella of the wood consists almost entirely of lignin. The primary layer of the wall is poorer in lignin, and the secondary layer contains still less lignin. In opposition to the views of G. J. Ritter (533), Freudenberg thinks that the lignin in the various parts of the wood is chemically all the same substance.

In order to avoid swelling of the wood, M. Staudinger (535) has altered Freudenberg's procedure by diluting Schweizer's solution with an equal volume of 25% ammonia. This solution dissolves only celluloses which have been extensively degraded. The solution proceeds without swelling. The cellulose is degraded with cold sulfuric acids of increasing strengths. In the first step the wood is treated with 6% acid; in the second, with 12%; in the third, with 24%; in the fourth, with 48%; and in the last, with 66% acid. The action requires several weeks. Even with this procedure a shrinking of the lignin structure could not be avoided; such a shrinkage seems unavoidable when the carbohydrate is dissolved out.

It was found that the distribution of lignin in the various layers was fundamentally different in the cases of hardwoods and softwoods. In the spruce and larch woods investigated the lignin permeates all of the "skeletal substance," but in the hardwood the lignin of the libriform fibers, which make up most of the wood, was found chiefly in the middle lamella. The lignin in the vessels was distributed as it is in the tracheids of softwood.

Experiments by W. M. Harlow (536) have shown that there are definite differences in the condition and distribution of the lignin in hardwood and softwoods. When the tracheids of softwood were treated with 72% sulfuric acid a cohesive residue of lignin was obtained; this was not the case with hardwoods. Hardwoods always gave a precipitate of finely divided lignin, which presumably was derived from the lignin of the cell walls. [According to M. Lüdtke (537) the enveloping layers of the primary and secondary lamellae behave like lignin in many respects, giving certain color reactions which are characteristic of lignin, and being easily attacked by oxidizing agents. However, they are not soluble in alkali after oxidation. Cf. however, R. Thiessen (538).]

A. J. Bailey (539) investigated the middle lamella of Douglas fir, using

a micromanipulator. He found that it consisted of 71% lignin, 14% pentosan, and 15% of an unknown substance. In contrast to Lüttke (537) he did not find that the middle lamella consisted of more than one layer. The lignin content in the wood rays was higher than that of the surrounding wood (540, 541).

It has already been pointed out that K. Freudenberg (300) distinguishes between *formed* and *unformed* lignin. The latter consists of lignin obtained by extraction with alcohol-benzene mixtures (lignin A), cold sodium hydroxide (lignin B), and especially with cold formic acid (lignin C). The lignin C is soluble in 66% sulfuric acid and in dilute alkali. It does not reduce Fehling's solution, even after cooking with dilute hydrochloric acid. The methoxyl content is 15%. Spruce wood contains 1-2% of this lignin.

The total amount of unformed lignin is approximately 4% of the weight of the wood (in spruce). The remaining 24% of lignin consists of the formed lignin, which is insoluble. This lignin shows the morphology of the woody tissue. Up to about 50% of the formed lignin is soluble in Schweizer's solution.

Beech wood contains only 12% of formed lignin, with a methoxyl content of 21%.

H. THE CONSTITUTION OF LIGNIN, BIOSYNTHESIS OF LIGNIN. LIGNIFICATION

Until the middle of the thirties there might still have been doubt as to whether lignin contained appreciable amounts of aromatic substances, since only about 10% of the weight of the lignin could be recovered in the form of aromatic products. On account of this and other facts, and especially because of the splitting off of methoxyl on treatment with 40-50% hydriodic acid after methylation and acetylation, H. Hibbert and H. W. Mackinney proposed for spruce lignin a formula which contained heterocyclic and pure aliphatic groups in addition to the aromatic constituents (542). This formula was, however, to be considered as hypothetical as those of many other authors.

The success of Freudenberg and his co-workers, [(421), cf. p. 279], in so conducting the degradation of isolated or native lignin with 70% potassium hydroxide at 170°C that subsequent methylation and oxidation yielded 20% of veratric acid and 12% of isohemipinic acid, represented a considerable advance.

These yields are equaled by those obtained by Freudenberg on oxidation of isolated lignin or spruce wood meal with nitrobenzene in alkaline solution; here as much as 25% of vanillin, some vanillic acid and vanillin-

carboxylic acid were isolated. Hibbert and his collaborators applied this method to maple lignin, and obtained approximately 15% of a mixture of vanillin and syringaldehyde.

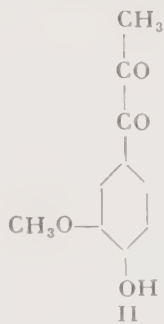
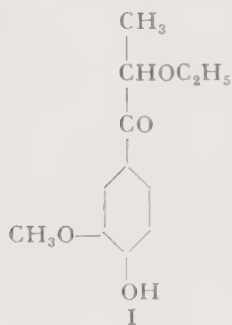
No less significant was the pressure hydrogenation of lignin in the presence of catalysts, first carried out at about the same time by Harris, D'Ianni, and Adkins, and later studied by Hibbert and his co-workers. Considerable quantities of hydrogenation products of the phenylpropane type were obtained.

This constituted a proof that the lignin molecule, whether it came from hardwood or from softwood, was probably built up of phenylpropane units.

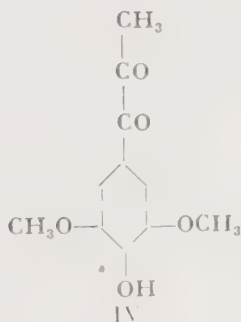
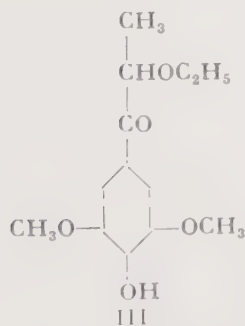
In view of these experimental results there is no point in discussing further the possibility that lignin might be an exclusively aliphatic substance.

The chief interest is focussed today on the question of the structure of the units derived from phenylpropane, and the manner in which these units are joined together in the lignin molecule.

One possibility which has experimental support is that the lignin units are related to the substances I and II, obtained by Hibbert (in small yields, to be sure) on ethanol-hydrochloric acid extraction of spruce wood:

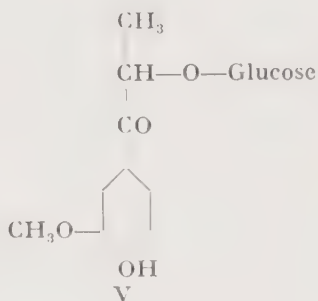


and also the substances III and IV, obtained from maple:



The occurrence of the isomeric primary keto alcohols in lignin may also be assumed.

The ethyl groups in I and III are derived from the ethyl alcohol used for the extraction; this may indicate that the substances are formed by alcoholysis of a glucoside (V), or by transesterification of substances of types X and XI (p. 309) with ethanol. The secondary alcohols corresponding to I and III react smoothly with ethanol-hydrochloric acid solution to give I and III (543).

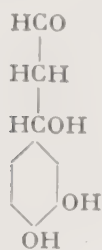


In consideration of these results, Hibbert had expressed the opinion that the compounds I-IV are the true building blocks of the lignin. His results had to be accepted with caution, however. It is true that these substances are resinified by the treatment with mineral acids which is employed to determine the lignin, and that they are therefore determined as lignin. This does not mean, however, that they are necessarily actual constituents of the lignin. It would, of course, also be possible that these substances, which always accompany the lignin, represent stabilization products of the precursors of lignin, which are formed during the biochemical synthesis of lignin. This view, expressed by H. Erdtman (544), has also been accepted by H. Hibbert (545). (Cf. page 323.)

These products of Hibbert could nevertheless very well be fitted into the ideas of the structure of lignin which have been developed by Freudenberg in the course of the years. According to Freudenberg (cf. for instance 546) the following pyrocatechol derivatives are substances which might possibly give lignin after condensation, ring closure, and methylation of the phenolic hydroxyls in *m*-position to the side-chains (Freudenberg at that time also thought that methylenedioxy groups might be present, but he has since abandoned this idea): dihydroxyphenylglycerol (VI), dihydroxyphenylhydroxypropionaldehyde (VII), and dihydroxyphenylacetylcarbinol (VIII).

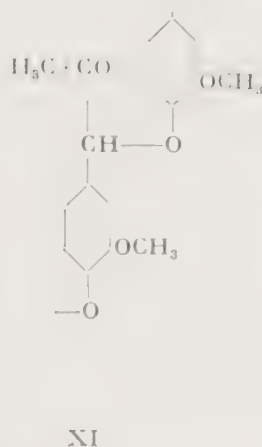
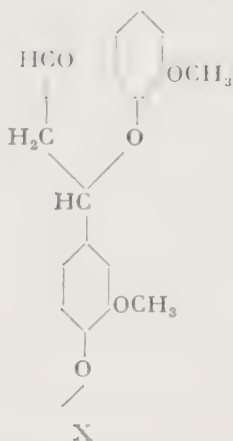
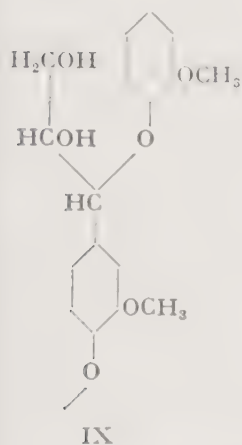


or
VII

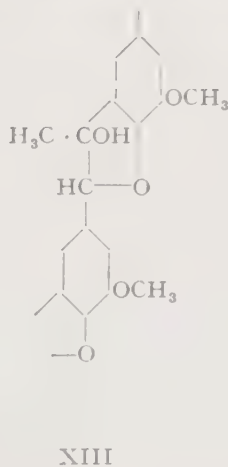
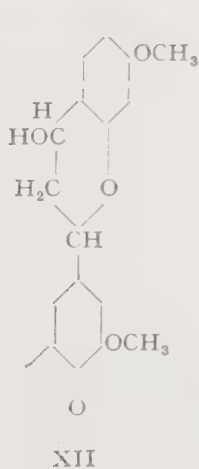


From a biogenetic point of view, these substances are equivalent to the Hibbert phenylpropane derivatives.

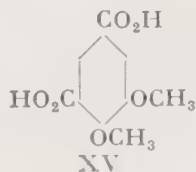
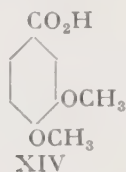
Etherification of the elements could proceed in the following way (IX, X, XI):



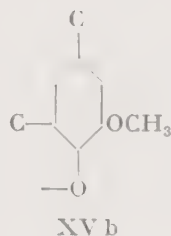
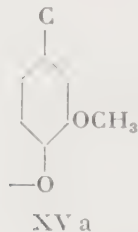
Intramolecular condensation of these compounds would in all cases lead to the benzopyran or benzofuran systems XII and XIII.



In agreement with his theory, K. Freudenberg found (468, 416, 103) that veratric acid (XIV) and isohemipinic acid (XV) are formed when wood or isolated lignin is heated with 70% potassium hydroxide, and subsequently methylated and oxidized with permanganate (cf. p. 277 and 279). The alkali treatment is assumed to break the non-cyclic as well as the cyclic ether linkages. The methylation then protects the phenolic hydroxyls which have been liberated.



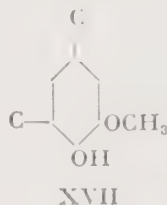
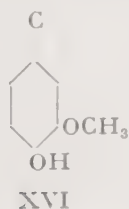
In this way Freudenberg obtained 20% veratric acid and 6-12% isohemipinic acid. The yield of isohemipinic acid could serve as a measure of the extent of C—C-condensed units as shown in XV b (cf. XII and XIII). The formation of isohemipinic acid, however, does not proceed quantitatively, so that estimates must be made. Freudenberg estimates that about 50% of the phenylpropane units are condensed by C—C-linkages in 5-position (547). This is in reasonable agreement with the fact, also found by Freudenberg and co-workers (122), that oxidation of lignin with nitrobenzene and alkali yields as much as 25% vanillin in addition to a few per cent of guaiacol, vanillic acid, and vanillin-5-carboxylic acid (cf. p. 280). Considering the losses of vanillin during the operation, Freudenberg states that the total yield of vanillin and related substances corresponds to about 50% of the phenylpropane units of spruce lignin. The aromatic nucleus in each of these units is bound to the side-chain of the next unit only by an ether linkage and not by a C—C-linkage (XV a).



As H. Erdtman (544) has remarked, it is not completely impossible that at least part of the isohemipinic acid may have been formed during the hot alkali treatment by secondary condensation between phenolic nuclei and side chains. This would make it still more difficult to draw quantitative conclusions from the yields of isohemipinic acid obtained.

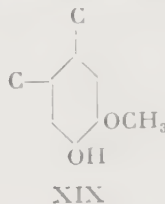
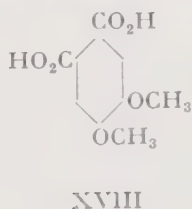
If spruce wood is methylated with diazomethane or dimethylsulfate and then oxidized with permanganate — without being heated with strong alkali — about 4% veratric acid (XIV) (based on the lignin content of the wood) can be isolated [E. Ungar (34)]. Similarly, permanganate oxidation of methylated hydrochloric acid lignin yielded 1-2% veratric acid [K. Freudenberg, F. Sohns, and A. Janson (412)]. The second characteristic oxidation product, isohemipinic acid (XV), was found only after hot-alkali treatment of the wood or the hydrochloric acid lignin, followed by methylation and permanganate oxidation, as described above. On the other hand, small amounts of isohemipinic acid (1.5-4%) in addition to veratric acid (2.5-6.5%), were obtained when certain lignin derivatives, such as alcohol lignin, acetic acid or thioglycolic acid lignin, or lignosulfonic acid, were methylated and oxidized (546, 548). These results were assumed to indicate that at least some of the oxygen linkages belonging to cyclic phenol ether groups, like those occurring in XII and XIII, had been opened during the preparation of these lignin derivatives.

Recently, H. Richtzenhain (548 a) has reinvestigated the permanganate oxidation of wood and isolated lignins. He was able to isolate isohemipinic acid also from the oxidation products obtained from diazomethane-methylated wood (0.9% of the lignin) and hydrochloric acid lignin (1.9%). This means a) that the genuine lignin contains a certain amount of phenolic groupings XVI, as well as XVII:



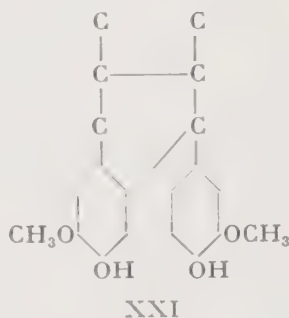
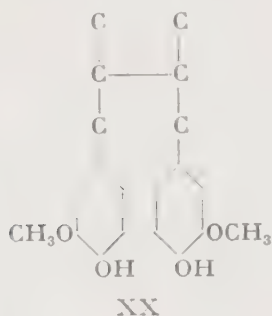
and b) that the splitting of cyclic phenol ether groupings, like those given in XII and XIII, need not be considered as an essential reaction in the formation of the lignin derivatives mentioned above.

Furthermore, Richtzenhain (548 a, b) has succeeded in isolating a new aromatic degradation product, namely metahemipinic acid (XVIII), from the mixtures obtained on permanganate oxidation of methylated hydrochloric acid lignin, ethanol lignin, and lignosulfonic acid.



These isolated lignins therefore contain the phenolic group XIX, in addition to groups XVI and XVII.

On permanganate oxidation of methylated wood, however, metahemipinic acid could not be detected. Obviously, the structure XIX has been formed from some other grouping, contained in the genuine lignin, during the preparation of the isolated lignins studied. Richtzenhain suggests that the genuine lignin possibly contains a certain amount of groups with the lignan structure XX, which, under the influence of the acids used in the preparation of the isolated lignins, are converted into the isolignan structure XXI.



On subsequent methylation and oxidation, the isolignan structure XXI would give metahemipinic acid. This rearrangement (XX \rightarrow XXI) would be in analogy to the well-known acid-catalyzed reactions in the lignan series, such as the rearrangements olivil \rightarrow isoolivil and lariciresinol \rightarrow isolariciresinol (cf. p. 341). This concept is also supported by the fact that no metahemipinic acid could be found on oxidation of (methylated) thiolignin, which, like wood, can not contain the groupings XXI, since it has not been exposed to the action of acids.

In the following table, given by H. Richtzenhain (548 c), the yields of the various aromatic products, obtained on permanganate oxidation of wood and isolated lignins, are summarized.

On the basis of the yields of metahemipinic acid, Richtzenhain estimates the amount of lignan or isolignan groups to be about 5% of all lignin units.

H. Richtzenhain (548 c) also discussed the question to what extent the yields of isohemipinic acid previously observed can be used as a measure of the frequency of guaiacyl propane units condensed in the 5-position [cf. also H. Erdtman (544)]. He points out that new units of this type, in addition to those already present in the genuine lignin, may be formed when wood is heated with alkali, by condensation of liberated guaiacyl propane units either with other lignin units, carbohydrates,

Lignin Preparation	Veratric Acid	Yields in % of the Lignin		
		Dehydro- diveratric Acid	Isohemipinic Acid	Metahemipinic Acid
Wood ^a	4.9	—	0.9	—
Hydrochloric acid lignin ^b	2.9	0.2	1.9	1.3
Lignosulfonic acid ^c	3.2	—	1.2	0.8
Ethanol lignin dissolved ^d	9.2	0.5	0.95	1.3
Ethanol lignin in the wood residue ^e	4.9	—	1.85	1.2
Hydrochloric acid lignin, after hot-alkali treatment	7.8	1.5	3.4	0.9
Thiolignin ^f	10.2	3.8	6.65	—

a Methylated with diazomethane, 12.97 % OCH_3 .

b Methylated with dimethylsulfate and alkali at room temp., 29.77 % OCH_3 .

c Isolated as lithium salt (11.31 % OCH_3 , 5.77 % S, $\text{OCH}_3\text{:S} = 1\text{:}0.48$) and methylated with diazomethane, 19.28 % OCH_3 .

d 21.08 % alkoxyl before, and 32.35 % alkoxyl after methylation with dimethylsulfate and alkali, calcd. as OCH_3 .

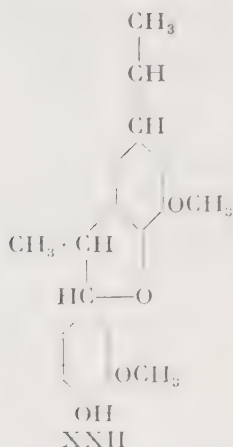
e Isolated as hydrochloric acid lignin from the alcoholized wood residue, 19.77 % alkoxyl before, and 34.43 % alkoxyl after methylation with dimethylsulfate and alkali, calcd. as OCH_3 .

f 13.58 % OCH_3 and 5.09 % S before, 30.66 % OCH_3 and 4.59 % S after methylation with dimethylsulfate and alkali.

or their transformation products. According to Richtzenhain, the previously estimated amounts of C_5 -condensed units lignin are probably too high.

In addition to the degradation products given in the table, Richtzenhain also obtained some succinic acid (0.5-1.0%) from all lignin preparations. Furthermore, methoxy acetic acid, $\text{CH}_3\text{OCH}_2\text{COOH}$, was isolated from hydrochloric acid lignin, lignosulfonic acid, and thiolignin, which proves the presence of primary carbinol groups, previously found by K. Freudenberg (448, 448 a) by means of analytical methods.

H. Erdtman (544, 121 f) has discussed the question as to whether the occurrence of five-membered (XIII) or six-membered (XII) oxygen rings is more probable. He points out that in naturally occurring, dimeric phenylpropanes, a C-C-linkage exists between the β -carbon atoms of the side-chains. This is true, for instance, for lignans such as pinoresinol, lariciresinol, and conidendrin (cf. p. 322 and 341). Furthermore, egonol (549) represents an example of a condensation between the β -carbon atom of one unit and the nucleus of the other. The same principle is also to be found in dehydrodiisoeugenol, which is formed by the action of mold enzymes or ferric chloride upon isoeugenol, and which, according to the work of H. Erdtman (550), G. Aulin-Erdtman (551), and K. Freudenberg and H. Richtzenhain (552), has the structure XXII.



Large groups of natural substances, comprising the anthocyanidins, the flavones, and the catechins which are also derived from phenylpropane, contain six-membered oxygen rings. In these compounds, however, the phenylpropane unit is condensed with an unsubstituted phenol and not with another phenylpropane unit.

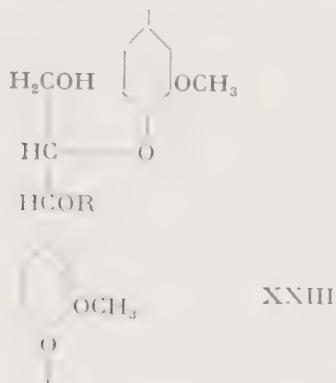
On the basis of these comparisons, the benzofuran system (XIII) would appear to be more probable than the benzopyran system (XII).

It is evident that there is a close similarity between dehydrodiisoeugenol (XXII) and Freudenberg's lignin unit XIII. Freudenberg found that a carboxylic acid (formula I, p. 200), which is derived from dehydrodiisoeugenol, reacts with sulfite cooking acid to form a sulfonic acid, which can be methylated and oxidized to isohemipinic acid and veratric acid. Freudenberg regarded these facts to constitute strong support to the existence of coumarane systems like XIII in the lignin.

Sulfite cooking of lignin was then believed to result in the splitting of coumaran rings. However, it was later found in Freudenberg's laboratory (106 b) that apparently no phenolic hydroxyls were liberated with increasing degree of sulfonation. Furthermore, H. Erdtman, B. Lindgren, and T. Pettersson (121) showed that hydroxyl groups disappear when sulfonic acid groups are introduced. These findings, as well as the spectrochemical data presented by G. Aulin-Erdtman (106 d) and the results of H. Richtzenhain mentioned above, indicate that the splitting of open or cyclic phenol ether linkages can not be an essential reaction in lignin sulfonation.

The investigations on the mechanism of the sulfonation of lignin, particularly the model experiments of B. Holmberg (112, 114), B. O. Lindgren (117 a) and H. Erdtman (121 f, 553) (cf. p. 202-210), have led to the assumption that sulfite cooking attacks α -phenyl carbinol

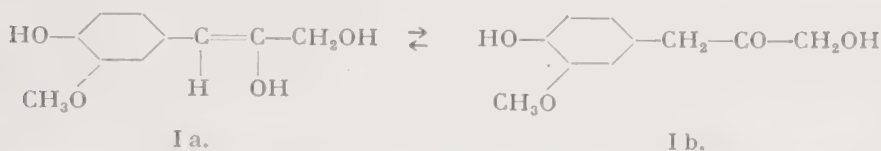
groups or their aliphatic ethers. Units which contain such sulfite-reactive groups may be tentatively illustrated by formula XXIII (cf. 117), where R can be a hydrogen atom (benzyl alcohol type) or a carbon atom of the side-chain belonging to an adjacent lignin unit (benzyl alkyl ether type):



Similar sulfite-reactive benzyl alcohol groups are present in the cyclic structures XII and XIII.

In addition, H. Erdtman has proposed the occurrence of another type of sulfite-reactive group, the cyclic acetals mentioned on p. 208.

A modification of Freudenberg's theory has been advanced by H. Hibbert. It is based on the theory that native lignin is derived from β -hydroxyconiferyl alcohol (I a) or its keto form (I b).

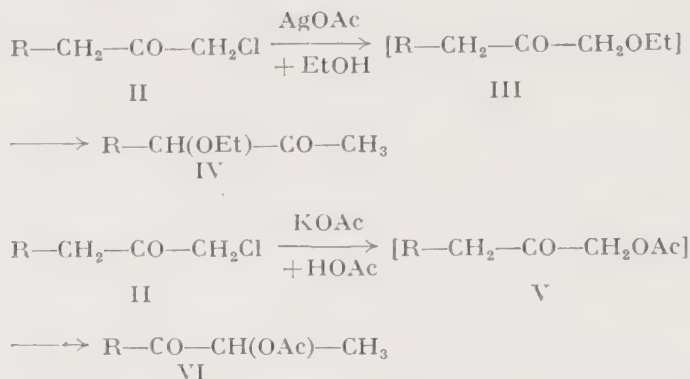


This substance is regarded by Hibbert (554) to be "the prime progenitor of native lignin."

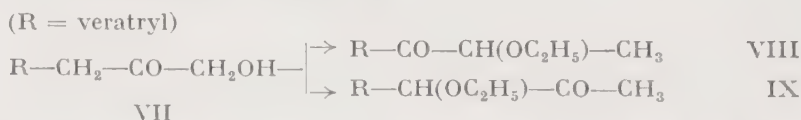
This idea has been supported by the finding that substances of this type on heating with 2% ethanolic hydrogen chloride give rise to the same monomeric products which previously had been obtained by ethanolysis of spruce and maple wood (cf. p. 241).

The β -hydroxyconiferyl alcohol is highly reactive; its synthesis was accomplished by H. E. Fisher and H. Hibbert (554) only after many unsuccessful attempts. Prior to this synthesis A. M. Eastham, H. E. Fisher, M. Kulka, and H. Hibbert (555) had tried to synthesize derivatives of β -hydroxyconiferyl alcohol which were methylated in the phenolic hydroxyl group and ethylated or acetylated at the terminal carbinol group. For instance, starting from the chloroketone II, which belongs to the veratryl series, reaction with silver acetate and ethanol was expected

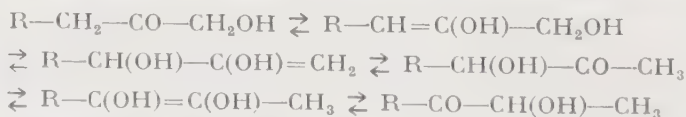
to yield the ether III, while the reaction with potassium acetate in acetic acid should give the acetate V. However, these normal reaction products were not formed, but rearrangements occurred, yielding the substances IV and VI:



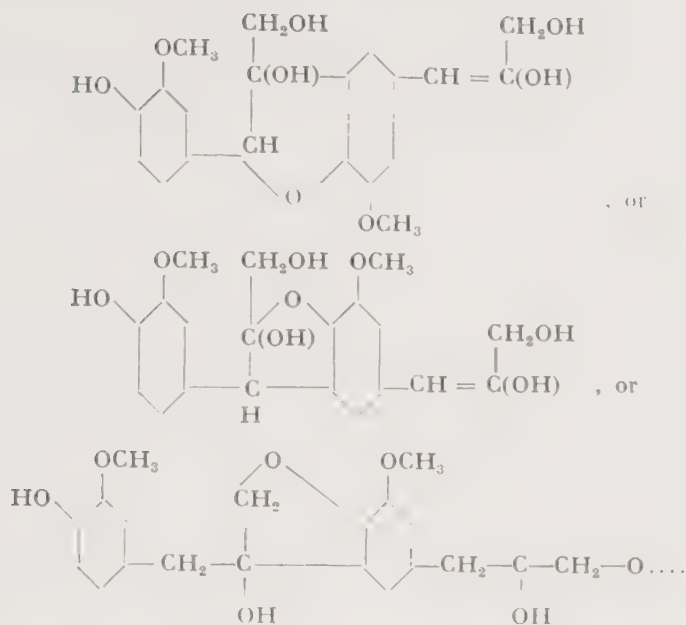
The formation of substances IV and VI represents a stabilization of the hydroxyconiferyl alcohol structure to the structure of Hibbert's ethanolysis products. The tendency toward stabilization was confirmed when it was shown that the β -hydroxyconiferyl alcohol methyl ether (VII), which was synthesized by H. E. Fisher, M. Kulka and H. Hibbert (556), on "ethanolysis" (heating with 2% ethanolic hydrogen chloride) yields a mixture of substances VIII and IX:



The occurrence of the guaiacyl analogs of VIII and IX among the ethanolysis products of spruce wood would thus find, according to these authors, "a satisfactory explanation in the assumption of their presence as stabilized end products arising from a more reactive native lignin building unit, namely, β -hydroxyconiferyl alcohol or its keto isomer." The authors assume that the highly reactive β -hydroxyconiferyl alcohol gives the following series of reversible rearrangements:

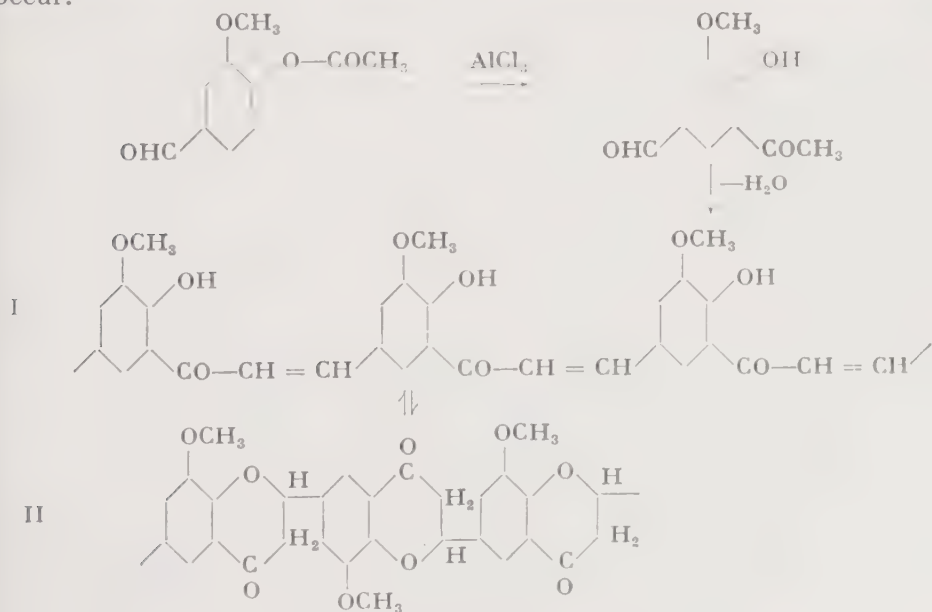


On the basis of the view, that β -hydroxyconiferyl alcohol is the progenitor of the native lignin and considering the finding (296) that native lignin does not contain any $-\text{C}-\text{CH}_3$ groups, Hibbert (555) proposed the following structures for lignin, which represent polymers of this progenitor, formed by three different mechanisms:



As Hilbert himself particularly emphasizes, these structural theories are also, like those of Freudenthal, highly speculative in character.

Some years ago, A. Russell (557) postulated a new structure for gymnosperm lignin and claimed further to have synthesized this lignin. According to his opinion, the behavior of lignin is in accordance with the structure of a polybenzopyranone (II). He tried to synthesize a substance of this type by heating acetylvanillin, dissolved in nitrobenzene, with AlCl_3 at 93-100° C for two hours. He assumed that the following reactions occur:



The methoxyl content of the synthetic product (II) was as low as 10%, which is only about two thirds of the methoxyl content of lignin. This is correctly explained by the demethylating action of aluminum chloride. Russell believes, that in all other respects, however, his product is the same as natural lignin.

The same lignin structure (II) has been proposed by D. M. Ritter, D.E. Pennington, E. D. Olleman, K. A. Wright and T. F. Evans (109). The evidence presented by these authors rests mainly upon the observation that methylation of lignosulfonic acid by diazomethane is favored by the presence of alkali, which should mean that alkali promotes the liberation of phenolic groups. It is assumed then, that these phenolic groups are liberated by a ring opening and that the ring involved has the benzopyranone structure.¹

There are, however, various reasons which make the benzopyranone (II) or chalcone structure (I) for lignin highly improbable. Some of these reasons may be mentioned here.

(1) Glading (481) has shown, that the ultraviolet absorption curves of flavanone and its corresponding chalcone (see formulas II and IV, p. 200) have distinct bands of high intensity at about 320 m μ , which are due to the carbonyl groups conjugated to the benzene nucleus [cf. also (479)]. This typical absorption is totally missing in lignin, which possesses a maximum at 280 m μ . Carbonyl groups in the benzopyranone position can, therefore, not be present in lignin in appreciable amounts.

(2) As Richtzenhain (105) has demonstrated, the flavanone ring is opened by heating with bisulfite cooking acid, yielding a sulfonic acid which contains a phenolic hydroxyl group (see formula III, p. 200); the same substance is formed by sulfonation of the corresponding chalcone. If lignin had one of the structures I or II (p. 317), the corresponding sulfonic acid would then contain at least one phenolic hydroxyl for every sulfo group. This is, however, not the case (see, for instance, p. 286). The formula of ligninsulfonic acid given by Ritter and co-workers (109), with the sulfo group in 3-position of an intact benzopyranone ring does not take account of Richtzenhain's model experiment; furthermore, it involves substitution of a hydrogen atom for $-\text{SO}_3\text{H}$, which is unreasonable.

(3) Methylation and subsequent oxydation of substances of the structures I and II would expect to give high yields of isohemipinic acid, in accordance with model substances of similar type. Lignin gives low yields of isohemipinic acid.

¹ *Note added in proof:* In a recent publication, D. M. Ritter, D. E. Pennington, E. D. Olleman, and K. A. Wright [*J. Am. Chem. Soc.* **72**, 1347 (1950)] have withdrawn their flavanone hypothesis.

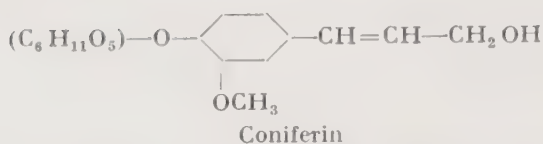
(4) It is well known that the native lignin is highly sensitive to acids. Heating of wood meal with a phosphate buffer of pH 2 is sufficient to make subsequent delignification with bisulfite cooking acid incomplete (cf. p. 423). Hydrochloric acid lignin can be sulfonated only if it is prepared under very mild conditions. It is unthinkable that native lignin would remain essentially unchanged by two hours heating with aluminum chloride at 100° C. The synthetic product which has been prepared by Russell under such conditions, can therefore not be similar to native lignin.

If the lignin *in situ* is high molecular, any proposed structures must take account of the fact that hydrolytic or alcoholic degradation of the lignin yields fragments of low molecular weight.

Such a breakup of the lignin structure occurs in many reactions, particularly during the digestion of wood with sulfites and certain organic reagents, including particularly the alcohols and lower fatty acids in the presence of mineral acids. This fact requires that an appreciable portion of the lignin be not condensed, but rather held together by labile ether linkages. During the extraction procedures, the splitting of these linkages competes with condensation processes (558, 559) with the result that the dissolving of the lignin frequently comes to a full stop. Under some circumstances the lignin already in solution can condense with that which has not yet dissolved; this occurs in burnt cook, which is sometimes observed during sulfite pulping. There is also no reason why the lignin molecules going into solution can not condense with others which are already in solution; this may be the explanation for the fact that the lignosulfonic acids in sulfite waste liquor can be divided into fractions with quite different molecular weights.

The views on the structure of lignin developed here are obviously not final. It is firmly established, in any case, that the fundamental constituents of lignin, whether from hardwood or from softwood, are aromatic. It is also certain that these fundamental constituents include guaiacylpropane units in the case of softwoods, and guaiacyl as well as syringylpropane units in the case of hardwoods, and that the units are bound together in various ways.

These main results appear to be in general accordance with the hypothesis advanced as early as 1897 by P. Klason (100), namely, that lignin is a condensation product of coniferyl alcohol (or a hydroxyconiferyl alcohol, or coniferaldehyde). Klason's hypothesis was supported by the previous finding of F. Tiemann and W. Haarmann (559 a) that coniferin, the glucoside of coniferyl alcohol, is present in the cambial sap of certain conifers.



Klason never succeeded, however, in obtaining convincing proof of his viewpoint. His indirect arguments, and the small yields of aromatic degradation products obtained by him, were not sufficient.

We do not yet know for certain what the *origin of the precursors of lignin* is. P. Klason (560) thought that it was probable that they might be formed from pentosan.

B. Rassow and A. Zschenderlein (561) point out that the lignin and pentosan contents of wood are in inverse relationship to one another; i.e., as the one increases, the other decreases, and vice versa. This is indicated not only by a comparison of different kinds of woods, but also by comparison of samples of the same type of wood of different ages (562). They assume, therefore, that there is a close chemical connection between lignin and pentosan, with the pentosan constituting at least one of the precursors of the lignin. The process of lignin formation is slower in hardwoods than in softwoods; this results in a higher lignin content in the latter.

W. Schrauth (563) also assumes that the lignin is formed from carbohydrate intermediates. In his opinion these intermediates consist not only of pentoses but also of hexoses.

A. Cleve-v. Euler (564) shares the opinion of Klason, that lignin is formed from pentoses or methylpentoses, with coniferyl alcohol as an intermediate. The further condensations, rearrangements, and other reactions are not the same in the leaves as in the stem.

In contrast to these views, according to which the lignin is formed by rearrangement of soluble carbohydrates, other investigators believe that lignin arises by secondary changes in the cellulose. This is indicated by Green's formula for lignin. J. König and E. Rump (508) are also of this opinion; they assume that lignin is formed by the addition of alkyl groups to the cellulose molecule, and should be regarded as a mixture of celluloses which have been methylated to various extents. P. Casparis (565) also thinks that lignin arises from the carbohydrates of the cell wall.

The formation of lignified cell walls from walls of pure cellulose, proceeds, according to W. Fuchs (566) through an intermediate stage in which the membrane contains *pectin*.

A. J. Bailey (567) asserts that the lignin and pentosan content of the middle lamella of Douglas fir is more than twice as great as that of the

remainder of the wood. This indicates a certain connection between the lignin and pentosan, especially in regard to the formation of lignin.

E. Beckmann, O. Liesche, and F. Lehmann (568) investigated winter rye straw in various stages of development, with a view to determining the dependence of the lignin formation on the state of growth of the plant:

	I ^a	II ^b	III ^c	IV	V	VI
Age in days.....	192	223	231	239	253	274
Ash content, %.....	8.37	5.12	3.59	2.61	3.23	2.55
% Lignin (Willstätter) ..	13.03	17.24	18.57	18.86	19.07	20.49
% CH ₃ O in lignin.....	3.03	11.46	13.41	12.84	13.38	13.42

a Stalks completely green, 22 cm. long, no formation of ears.

b Stalks still slightly green, 130 cm. long, ears 11 cm. long. Four weeks of hot weather had intervened between I and II.

c From this point on the length of the stalks remained constant at 155 cm.

From this table it may be seen that the content of lignin is dependent on the age of the plant. The formation of lignin begins very early; even in very young shoots the lignin content was 11.6%. It has often been found that the lignification of young tracheids occurs while the cells are still alive; the helical ridges are the first to be lignified, while the membrane consists of pure cellulose. The lignification ceases with the growth of the cell (569).

The table also shows that the methoxyl content of the lignin is very low at the beginning, but increases rapidly. From this fact, it might be possible to consider the methylation of the lignin as a secondary process: a methoxyl-free lignin is presumably formed at first.

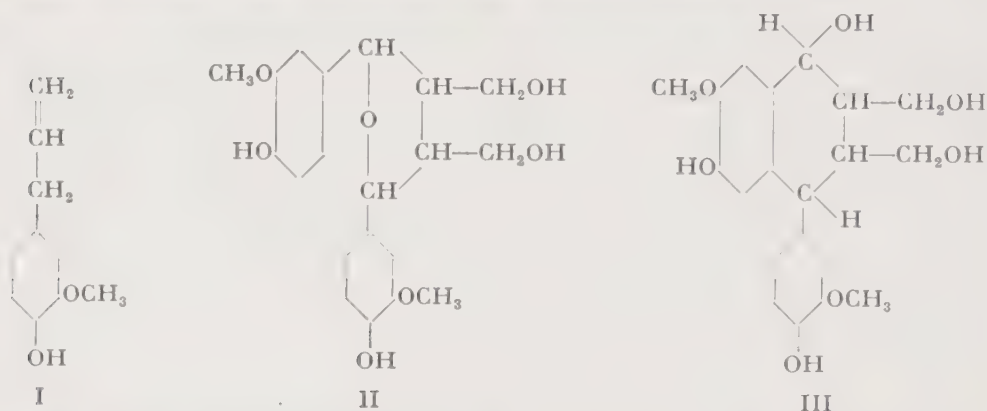
M. Phillips and M. G. Goss (570) investigated the composition of barley stalks and leaves at various stages of development, and found, in agreement with E. Beckmann, that both the lignin content and the methoxyl content of the lignin increased regularly during growth. When the plant ripened there occurred a rapid increase in lignin content, and a rapid methylation of the lignin. From these results they conclude that no building materials for the lignin are derived from the cellulose or from pentoses or pentosans, but that they come from other soluble sugars (571).

F. Tobler (572) found that in a disease of hemp, which was presumably due to metabolic disturbances, the bast fibers were normal, but the cells of the woody tissue were quite incompletely lignified. The development appeared to stop at an incomplete stage, with *cellulose* and *pectin* taking the place of the lignin.

B. L. Vanzetti (573) has developed a completely different concept of the biogenesis of lignin. He believes that substances with the structure of olivil are the precursors of lignin. Under normal conditions they give rise to lignin, and under pathological conditions, to resin.

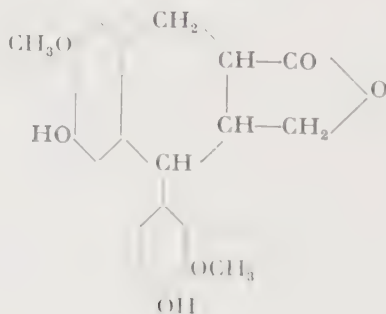
The synthesis may be thought of as beginning with the formation of compounds of the type of eugenol (I). Condensation of two such molecules would give olivil (II), and ring closure would then produce isoolivil (III) (574), substances belonging to the group of *lignans* (cf. p. 339). Finally, oxidation and further condensation or polymerization, presumably with compounds of the type of the so-called *sulfite liquor lactone* (condendrin), would yield lignins or resins.

This idea is based upon the fact that the wood of olive trees does not normally contain any resin. Under pathological conditions, however, liquid resins arise, which ooze out between the wood and the bark. Under some circumstances olivil crystallizes out of the resin directly.



The sulfite liquor lactone was first observed by J. B. Lindsey and B. Tollens (575) when they extracted the sulfite waste liquor with ether. B. Holmberg (576) investigated it further, determining the empirical formula $C_{20}H_{20}O_6$, and finding that it was a lactone. He also discussed the structure of this sulfite liquor lactone. Further investigations by H. Erdtman (577) [cf. also R. D. Haworth and G. Sheldrick (578)] have shown that it is a phenylnaphthalene derivative.

According to S. Keimatsu, T. Ishiguro, and G. Yamamoto (579) it is identical with tsugalactone or tsugaresinol, which is obtained by ether extraction of the wood of *Tsuga Sieboldii*. Its formula is:



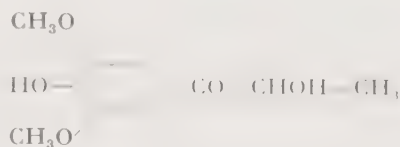
It is evident that this substance is closely related to isoolivil. They both belong to the group of natural products which can be derived from 1,4-diphenyl-*n*-butane, and can be regarded as dimeric coniferyl compounds.

B. Holmberg studied this substance with great care, since he thought for a while that it was a precursor of lignin, or a stabilization product of one of the precursors of lignin.

It should further be mentioned that H. Hibbert (580) believed that the lignin units which he obtained by alcoholysis, namely α -hydroxypropio-guaiacone (I) and α -hydroxypropiosyringone (II), or their dismutation products serve as respiratory catalysts. Only after death are they polymerized to larger complexes. In the case of wood, the polymerization does not proceed far, and leads to a product which is extremely sensitive to chemical attack and is hence easily altered.



I



II

The proposal by H. Hibbert that lignin is derived from β -hydroxy-coniferyl alcohol has already been discussed on p. 315.

H. Erdtman (581, 553) regards the enzymatic dehydrogenation of monomeric phenolic building units as the basic principle in the biological formation of high polymeric lignin. The free radical character of phenol dehydrogenation would readily explain the fact (582) that both the dehydrodiisoeugenol (p. 314), which has been prepared from isoeugenol by the action of mushroom oxidase, and the lignins are optically inactive, in spite of the presence of asymmetric carbon atoms. Only the primary step, i. e. the dehydrogenation of the phenolic monomer to a radical, is assumed to be an enzymatic process. The following polymerization (etherification and condensation) of the radicals proceeds spontaneously.

K. Freudenberg and H. Richtzenhain (583) have measured the oxygen consumption, which took place when mushroom oxidase preparations were allowed to act on various model substances belonging to the guaiacyl and syringyl series, as α -hydroxypropiovanillone, coniferyl alcohol, vanillin, vanillic acid, and several others. In some cases the reaction products were isolated. They were amorphous, polymeric substances, which had been formed partly by reactions involving the loss of phenolic hydroxyl groups and the formation of ether linkages, i. e., reactions quite similar to those which are assumed to occur in lignin formation.

Quite recently, K. Freudenberg (583 a) reported that the product obtained by the action of mushroom phenol oxidase upon coniferyl alcohol exhibits several properties similar to those of lignin. It is an amorphous, thermoplastic, and optically inactive substance, which shows the color reactions of lignin (coniferyl aldehyde groups, cf. page 188), gives 95% "Klason lignin", and contains only few free phenolic hydroxyl groups. On sulfite cooking, it is converted into a sulfonic acid which gives the same ultraviolet absorption curve as lignosulfonic acid. When heated with mineral acids, it splits off formaldehyde, similar to lignin.

The infrared spectrum of the polymeric dehydrogenation product of coniferyl alcohol proved to be very similar to that of the "native lignin" of F. E. Brauns. The molecular weight of the synthetic product is reported by Freudenberg (493 a) to be about 900. This is similar to that of a methyl lignin extracted by Freudenberg from methylated wood by means of cold formic acid containing 0.5% hydrogen chloride (cf. p. 297). The synthetic product is soluble in alkali and several organic solvents and is also in this respect comparable to Brauns' "native lignin". Upon treatment with hot, dilute mineral acids, it becomes insoluble and is then, according to Freudenberg, comparable to cuproxam lignin, which is also insoluble and has also been exposed to the action of boiling dilute acid.

Using 3,4-dihydroxy-phenylalanine as a substrate, the presence of a phenol oxidase in the living tissue of wood could be demonstrated.

According to a study of K. Kratzl (584) light energy is not necessary for the formation of lignin. He found, in contrast to a previous statement of P. Klason (585) that potato germs grown in the absence of light contain a substance which on the basis of microscopic staining observations and chemical analysis can be classified as lignin.

I. THE DETERMINATION OF LIGNIN

1. Isolation with Strong Acids

a. Sulfuric Acid. P. Klason (586) was the first to attempt the determination of lignin in spruce wood by treating the wood with 70% sulfuric acid. This method is based on the assumption that lignin is completely insoluble in this acid, and that the cellulose and the other carbohydrates dissolve completely. Under the conditions which he employed, this is practically correct in the case of spruce wood. From this fact the opinion arose that lignin was in general insoluble in mineral acids, since it could not be "saccharified." Indeed this supposed property was even used as a definition of lignin.

In the course of time, however, it was found that lignin was not under all circumstances insoluble in mineral acids. Under certain conditions it is possible to dissolve appreciable amounts of lignin in acid.

Another difficulty in the determination of lignin with strong mineral acids is the fact that the carbohydrates which first go into solution are sometimes converted to humus, and thus cause too high a value to be obtained for the lignin content.

Finally, it was found that when sulfuric acid was used, the lignin took up some acid which had to be removed before the lignin was weighed. When the method was tested, softwoods (especially spruce) were usually used. In the case of spruce wood it is quite true that the sulfuric acid method, properly employed, gives useful results.

This is also evident from the investigations of K. Freudenberg and T. Ploetz (587). They used Klason's method (588) and tried to find out the best concentration of acid for obtaining reliable values for the lignin. It might have been predicted that too low concentrations of acid would leave polysaccharides in the lignin, while too high concentrations would cause the formation of humus. In both cases the lignin values would be too high. This may be seen from the following figures.

Spruce Wood

Concentration of sulfuric acid, %	62.5	66.5	70.5	75.0	80.5
Yield of lignin, %.....	30.1	26.3	26.2	26.2	29.9
Methoxyl content of the lignin, %	14.8	15.6	15.9	16.1	13.4

The lignin values are practically constant over a fairly wide range of sulfuric acid concentrations, from 66.5% to 75%. The methoxyl content of the lignin increases from 15.6 to 16.1%, however. According to these authors a maximum methoxyl content indicates that the lignin is pure; this factor must be controlled, therefore, during the determination. The result of these studies, is then, that 75% sulfuric acid should be used when the lignin in spruce wood is determined by the method of Klason.

Circumstances are not so favorable for the determination of lignin in hardwoods, straw, and similar materials (589). When the investigations of Freudenberg and Ploetz were extended to linden and beech woods, the following results were obtained:

Linden Wood

Concentration of sulfuric acid, %	62.5	66.5	70.5	75.0	80.5
Yield of lignin, %.....	20.0	21.5	22.4	25.3	34.1
Methoxyl content of the lignin, %	17.4	19.6	20.1	20.4	12.8

Beech Wood

Concentration of sulfuric acid, %	61.7	66.4	70.5	74.9	78.0
Yield of lignin, %.....	23.9	22.3	23.4	26.9	33.2
Methoxyl content of the lignin, %	20.7	21.8	20.2	18.4	13.8

It will be observed that no minimum yield of lignin is obtained from linden, while beech gives a rather ill-defined minimum with 66.4% sulfuric acid. This minimum coincides with a maximum methoxyl content. In the case of linden, the maximum methoxyl content is found with 75% acid.

These results make it more evident than ever that, as Ploetz has emphasized, this method of determining lignin will always be a "conventional" method. With spruce wood one can obtain reproducible results over a wide range of acid concentrations, but the lignin values obtained with hardwoods, straw, and such materials are very uncertain.

As far as the details of the procedure are concerned, one must be particularly careful to carry out the acid treatment with material which is sufficiently finely divided. Rapid and complete wetting is also important; this can easily be achieved by digesting with acid in a vacuum, as E. Hägglund and co-workers (590) have proposed (especially when lignin was determined in softwoods or softwood pulps). This removes the air which prevents the penetration of the acid. The procedure is as follows:

One g. of air-dry material—sawdust or defibrated pulp—which has been extracted for 6 hours with acetone in a Soxhlet, is treated with 10 cc. of 72% sulfuric acid (d. 1.64). The temperature is kept down to room temperature. The mass is stirred with a glass rod, put in a desiccator, and the air removed by two or three evacuations. After 4 hours the mixture is diluted with 25 cc. of water, and allowed to stand for 4 hours more at room temperature. The solution is then transferred to a flask, diluted with 320 cc. of water, and refluxed for 6 hours. The lignin is filtered off, dried and weighed. The material thus saccharified amounts to 107-109% of the weight of the lignin-free material when wood is used and 109-112% when cellulose is saccharified. These figures indicate that the saccharification proceeds quantitatively and that no humus is formed. If the sulfuric acid mixture is allowed to stand 48 hours or longer there is great danger of decomposition; R. S. Hilpert and E. Littmann (591) have called attention to this fact. Hägglund and his collaborators have furnished experimental evidence showing that the procedure described above does not lead to decomposition of sensitive sugars like xylan [cf. also A. G. Norman (592)].

According to W. Jensen (592 a), Hägglund and co-workers' method will yield the most correct lignin values if the following sulfuric acid concentrations are used: for pine 72%, for spruce 71%, for birch 71%. The same author has also studied the influence of the extraction solvent upon the lignin value, and concluded that pre-extraction with ether is most satisfactory in the case of spruce, while acetone is most suitable in the case of pine.

In the method of Noll and his co-workers (593) the reaction time is decreased by the addition of tertiary amines like dimethylaniline, pyridine, or quinoline. These compounds are supposed to accelerate the esterification of the cellulose with sulfuric acid. The fact that Noll used 78% acid instead of 72% must also have had some effect on shortening the time. The time was decreased to a few minutes. The material (1-3 g. in the case of cellulose) in the form of a fine, dry powder, is moistened with 5-8 cc. of pure dimethylaniline, and then treated with 25-35 cc. of 78% sulfuric acid. When the cellulose has been completely dissolved, the mixture is poured into 200 cc. of hot water, and boiled for 5 minutes. The lignin is then filtered off, dried, and weighed.

When it is necessary to make quantitative determinations of *very small amounts* of lignin, as in the case of soft or bleached pulps, A. Noll (594) dilutes with 80% alcohol instead of water; this gives a resin-free residue.

In some cases a method is used which is an improvement of one first suggested by P. Klason, namely, the colorimetric determination of the dark color obtained when wood is digested with 78% sulfuric acid. The solution is more or less darkened, depending on the lignin content, and the lignin can thus be determined by comparison with standard samples which are treated simultaneously, and whose lignin contents have been determined in other ways.

E. Hägglund and H. W. Giertz (595) have considerably improved and extended the methods for the colorimetric determination of lignin in bleached pulps.

The wood may not be extracted with hot water or with dilute hot acids before the lignin determination, because a part of the lignin will be dissolved (cf. p. 105) (596).

For further literature concerning the determination of lignin with sulfuric acid see ref. 597.

b. Hydrochloric Acid. The use of hydrochloric acid for the determination of lignin is much more difficult than that of sulfuric acid. There is also more danger that the dissolved carbohydrates will be converted to humus. The carbohydrate may be separated from the lignin either by treating the wood with a large excess of very concentrated hydrochloric acid, or by passing hydrogen chloride into wood which has been moistened with water (cf. p. 402).

In the first case (397), finely ground wood which has been exhaustively extracted with ether or acetone is shaken in a glass-stoppered flask with 20-30 times its weight of approximately 43% hydrochloric acid. After the mixture has stood for 24 hours at room temperature, it is treated with water and filtered. The lignin is freed of acid by washing with water

to which a little soda has been added, and is dried at 105°C and weighed. The weight is corrected for the ash content. If no soda is used, 1.63-2.5% of chlorine ion remains in the lignin despite thorough washing [cf. Ungar (34), and Hägglund (356)].

Contact with the concentrated hydrochloric acid causes a considerable amount of lignin to go into solution at first, but it later precipitates out again (598). It is necessary to wait until the lignin has finished reprecipitating before filtering it off. One makes sure that no lignin remains in solution by diluting the filtrate ten times, and cooking it for several hours.

The isolation of the lignin by treating the damp wood with hydrogen chloride gas is carried out as follows (599): The extracted sawdust is rubbed up with 3-6 times its weight of water, and hydrogen chloride is passed into the mixture until it becomes quite thin. (The mixture is cooled in ice while the hydrogen chloride is being led in.) After 24 hours the solution is diluted with water, and cooked for several hours. The lignin is then filtered off and weighed.

c. Hydrogen Fluoride. O. Eichler (600) and W. Klatt (601) attempted to determine the lignin content of wood with hydrogen fluoride, basing their experiments on the solution of cellulose with hydrogen fluoride, carried out by B. Helferich and S. Böttger (602), and by K. Fredenhagen and G. Cadenbach [(603) (cf. p. 101) K. Wiechert (604) extended the experiments, and worked out the following method:

The pre-extracted wood is carefully dried and then repeatedly digested with cold, liquid hydrogen fluoride, necessarily in special apparatus. The carbohydrate is rapidly dissolved. The solution is sucked off and the lignin which remains behind is treated with 2% hydrochloric acid, washed, and dried. In the case of softwoods, the hydrogen fluoride may be used at a temperature of approximately -10°C , but this degree of cooling is not sufficient for hardwoods, because part of the lignin will then be dissolved too. If the reaction mixture is cooled to about -60°C with dry ice, only the carbohydrate is dissolved. Humus formation will not occur under these conditions, partly because the material is in contact with the hydrogen fluoride for so short a time (approximately 30 minutes).

This method sometimes gives lower values for the lignin than do the sulfuric and hydrochloric acid methods as carried out by W. Ender and O. Uebel (605), or by E. Heuser and K. Skiöldebrand (368).

d. Mixtures of Strong Acids. Since it is sometimes inconvenient to work in the laboratory with fuming hydrochloric acid, the use of mixtures of ordinary concentrated hydrochloric acid with sulfuric or phosphoric acids has been proposed. V. Hottenroth (606) patented the use of mixtures of

hydrochloric and sulfuric acids for the saccharification of cellulose. R. Willstätter (607) found that this method is not so suitable for the isolation of lignin as the use of highly concentrated hydrochloric acid. However, L. Kalb's (608) method of determining lignin is based on the use of a mixture of 2 liters of concentrated hydrochloric acid (d. 1.18) and 500 g. of 95.6 % sulfuric acid; 20 cc. of this mixture is used for 1 g. of material. The reaction mixture is shaken violently at first, then allowed to stand for 24 hours, diluted with 100 cc. of water, boiled for 10 minutes, and filtered. A correction is usually made for the ash.

H. Wenzl (609) adds phosphorus pentoxide to the hydrochloric acid, using 30 g. of the pentoxide to 100 cc. of hydrochloric acid (d. 1.19). This supposedly increases the hydrolyzing action of the acid.

H. Urban (445) likewise isolated lignin with mixtures of hydrochloric and phosphoric acids. 30 g. of wood was treated for 44-62 hours with 1,350 cc. of hydrochloric acid (d. 1.18) and 450 cc. of phosphoric acid (d. 1.7). The yield of lignin from spruce was surprisingly low, being only about 25 %. This indicates that part of the lignin was dissolved. The method is evidently suitable only for preparative purposes.

e. Hot, Dilute Mineral Acids. J. König and E. Rump (350) determined the lignin by pressure heating the wood with 1 % hydrochloric acid for 6-7 hours. This method involves certain difficulties in obtaining suitable apparatus.

J. König and E. Becker (610) determined the lignin content of various woods by four of the methods given above, and compared the results. As the following figures show, the agreement of the values obtained for the same kind of wood is quite satisfactory, with a few exceptions.

Per Cent of Lignin

Kind of Wood	1% Hydrochloric Acid, Heated 6-7 hours at 6 atm.	72% Sulfuric Acid Klason's Method	Highly Concentrated Hydrochloric Acid	Hydrogen Chloride, Method of Dangevilliers and Krull
Fir.....	29.94	28.81	29.36	29.17
Fir.....	28.91	28.10	28.04	27.98
Pine.....	29.52	29.56	31.33	29.16
Birch.....	23.54	22.55	20.96	23.27
Birch.....	27.28	26.36	26.75	26.38
Poplar.....	22.14	22.36	22.06	22.45
Poplar.....	21.00	21.06	21.91	20.75
Beech.....	22.07	22.90	23.99	22.69
Ash.....	26.71	25.90	19.59(?)	26.01
Willow.....	25.06	25.97	24.54	24.70
Alder.....	25.95	23.04	23.05	24.57

2. Indirect Methods for Determining Lignin. There are no completely reliable methods for carrying out exact indirect determinations of lignin.

There are, however, several relatively simple methods for obtaining approximate values of the lignin content. These methods are based on determinations of methoxyl, or on measurements of the chlorine or bromine consumptions of wood, or the amount of phloroglucinol it takes up.

The determination of the methoxyl according to Zeisel can be made very exactly, and quite rapidly. If the methoxyl contents of the lignin of all kinds of wood were equal, and if all of the methoxyl of the wood were attached to the lignin molecules, this would be an excellent method for determining the lignin content of woody tissues. Such is not the case, however. We now know that an appreciable amount of the methoxyl is attached to the carbohydrate, and also that the methoxyl contents of the lignins of various woods differ considerably.

G. J. Ritter (611) found that large amounts of methoxyl were split off during the isolation of lignin. This fact is apparent from the following table.

Kind of Wood	Lignin in Wood (a), Determined with 72 % H ₂ SO ₄	Methoxyl Content of Wood (b)	$\frac{b}{a} \times 100 =$ Methoxyl Content of Original Lignin	Methoxyl Content of Isolated Lignin	Methoxyl Split During Isolation, in % of the Lignin
	%	%	%	%	
Western yellow pine.....	26.75	4.45	16.64	13.13	3.51
Western white pine.....	24.30	4.47	18.40	15.10	3.30
Incense cedar.....	37.68	6.09	16.16	14.51	1.65
Mesquite.....	30.77	5.49	17.84	14.05	3.79
Tan oak.....	24.68	5.70	22.06	16.99	5.07
Eucalyptus.....	26.74	6.56	24.53	15.01	9.52
Yellow poplar (sapwood)...	23.86	5.89	24.69	17.00	7.69
Yellow poplar (heartwood)...	23.69	6.03	25.45	20.22	5.23
Pignut hickory (heartwood)	22.85	5.79	25.34	18.43	6.91

It is possible to remove the larger part of the easily split methoxyl of the carbohydrate by treating the wood with 10 % sodium hydroxide. If the methoxyl content of the residue is then determined, it is possible to estimate the lignin content if one knows the methoxyl content of the lignin. L. Kalb (612) used his method to isolate the lignin from a series of lignified substances, and found the following values:

Methoxyl Content of Hydrochloric Acid Lignins

Source of Lignin	% CH ₃ O
Spruce.....	15.87
Pine.....	15.69
Beech.....	21.91
Oak.....	21.86
Ash.....	21.93
Almond.....	22.01
Peach.....	20.07

It will be seen from this table that the methoxyl content lies between 15 and 16 % in the case of softwoods, and between 20 and 22 % in the case of hardwoods.

One is justified in asking if these figures are not too high. It is not possible to avoid extensive condensation of the lignin when it remains for a long time in contact with strong acid. This condensation involves the loss of water, and consequent increase in the methoxyl content.

Investigations of E. Hägglund and O. Sandelin (81) showed that the methoxyl of the carbohydrate amounted to 0.56 % of the weight of the spruce wood. The wood itself had a total methoxyl content of 4.60%. This means that 4.04 % constituted the methoxyl bound to the lignin, and since the lignin (determined with hydrochloric acid) amounted to 27.2 % of the weight of the wood, the methoxyl content of the lignin was $(4.04/27.2) \cdot 100 = 14.8$ %. This is the value found for pure spruce lignin which has not been treated too violently with acids (613). E. E. Harris, E. C. Sherrard, and R. L. Mitchell (452) found that 88 % of the total methoxyl present in spruce wood belonged to the lignin. This agrees very well with the values found by Hägglund and Sandelin [cf. also G. J. Ritter and J. H. Barbour (614)].

P. Waentig and E. Kerenyi (615) have introduced the *chlorine* number as a measure of the lignin content. This also gives only an approximate value for the lignin. It has already been explained that lignin takes up large quantities of chlorine and other halogens.

Finely divided, moist wood from which the resin has been removed is treated with a stream of dry chlorine gas until it ceases to gain in weight. Excess chlorine is removed in a slow current of air, and a final weighing is then made. The percentage increase in weight is designated as the *chlorine* number. When this number is multiplied by the factor 0.71, the approximate lignin content of the wood is obtained (in per cent), since the *chlorine* number of the lignin itself is 140.

The *uptake of bromine* is also used for an indirect lignin determination. A. Tingle (616) used a bromine solution consisting of 8 g. of bromine in 100 cc. of normal NaOH, diluted to 1 liter. The lignin-containing material is finely divided, and pulped with a mixture of hydrochloric and sulfuric acids. This requires only a few minutes. The bromine solution is then added, and after $\frac{1}{2}$ hour the unused bromine is treated with potassium iodide, and the iodine liberated is back-titrated with thiosulfate.

K. Kürschner and K. Wittenberger (617) have proposed the determination of lignin by measurement of the quantity of bromine taken up from bromine vapor. They assumed that only double bonds in the lignin were involved, since bromine is taken up even in the dark (618).

The procedure is as follows: An exactly weighed amount of bromine is sealed into a glass vial, which, along with the lignified material, is put into a flask with a ground-in funnel. The flask is pumped free of air, and the glass vial is broken. The vacuum causes the bromine to be converted into vapor immediately. The reaction with the lignin is carried out in the dark. After approximately $1\frac{1}{2}$ hour, a potassium iodide solution is added, and the iodine is titrated with thiosulfate.

The ratio between the per cent of lignin and the halogen number turned out to be a constant for each individual group of lignified substances. The value of this constant must be known if the lignin content is to be calculated. This makes it necessary to determine the lignin content by one of the familiar methods. Wiechert has rightly remarked that an acid hydrolysis is most suitable.

If the variation in the halogen number from group to group of lignified substances did not occur, this would be a very simple method for determining lignin.

The third indirect method for the determination of lignin was reported by C. F. Cross, E. J. Bevan, and J. F. Briggs (619). It is based on the previously discussed property of lignin of condensing with definite quantities of phloroglucinol in hydrochloric acid solution. The phloroglucinol not consumed is titrated with a formaldehyde solution, or precipitated with furfural as furfural phloroglucide, and weighed (620). M. Neumann (621) and W. Fuchs (622) recommend determining the excess of phloroglucinol by titration with diazotized *p*-nitraniline. [Cf. also R. Sieber (623)].

V. Minor Components of Wood

A. RESIN, TERPENES, AND FAT

By resin (i.e. natural resin) one does not mean a uniform substance, but rather a complicated mixture of solid or semisolid materials which are formed in certain woody tissues. These substances consist only of carbon, hydrogen, and oxygen, and are characterized by their insolubility in water, by their relative inertness toward chemical reagents, and by their solubility in ether, alcohol, benzene, and other organic solvents to form gummy solutions (624). We do not yet know what biochemical processes are involved in the formation of resin. A distinction is made between *physiological* and *pathological* resin. The former arises during normal growth inside the tissue, and remains there, while the latter is formed as a result of injury to the bark (oleoresin).

Resins occur very widely distributed in the plant kingdom. Besides the resin contained in intercellular passages (resin channels) resins also occur in the interior of the cells and in the cell walls. The bark and the wood of certain types of trees are particularly rich in resin [cf. Wiesner (625)].

The resins which flow from fresh wounds in coniferous trees, the so-called *balsams* or *oleoresins*, are soft, because the solid resin acids are partly dissolved in turpentine, forming a paste. The content of turpentine can vary widely. While H. Mayr (626) reports the turpentine content of balsam from conifers as 32-60%, P. Klason and J. Köhler (627) found only approximately 7% in spruce resin. H. Bergström (628) obtained the following yields:

Alcohol-Ether Extract from Trunks of	% of the Weight of the Wood		% Turpentine in Extract
	Resin and Fat	Turpentine	
Pine.....	6.0	0.35	5.5
Spruce.....	2.3	0.05	2.1

The values reported by G. Austerweil and J. Roth (629) may be compared with the above figures. The yields from the trunks or roots of the following trees are given in per cents of the weight of the wood.

Type of Wood	Turpentine	Non-volatile solids
White pine.....	0.75-1.75	4-7
Austrian pine.....	1.0-2.5	8-13
Fir.....	0.2-0.3	1.5-2.1
Spruce.....	0.2-0.4	1.7-2.2

H. Bergström and O. Fagerlind (630) obtained larger amounts of turpentine (20%) from extracts of roots. The wide variations in the compositions of the balsams appear to be due to the volatility of the terpenes.

The composition of the turpentine is not always the same. The oil from spruce and pine consists, according to O. Aschan (631), of 15-20% pinene, 25-30% dipentene, and 15-20% sylvestrene.

H. Bergström (632) investigated the turpentine from spruce and pine. The spruce turpentine was levorotatory and consisted of *l*-pinene and *l*-limonene, while that from pine was dextrorotatory and contained *d*-pinene, *d*-sylvestrene, and *d,l*-limonene (dipentene).

The presence of sylvestrene was formerly assumed in certain vegetable oils, like pine-needle oil, because sylvestrene hydrochloride is formed with hydrogen chloride. It has now been demonstrated, however, that sylvestrene is not present in these oils, but is formed by rearrangement of the Δ^3 - and Δ^4 -carene, either by heat or by the action of certain chemical agents; this explains its presence in sulfate turpentine (632 a).

American authors have made many investigations of the composition of balsams. Some of their results are given in the following table (633):

Kind of Wood	Constituents of the Turpentine	Resin	Author
<i>Pinus Jeffreyi</i> ...	<i>n</i> -Heptane (chiefly)	Contains 12.5 % of resenes	A. W. Schorger (634)
<i>Pinus monophylla</i>	85 % <i>d</i> - α -Pinene, 4-5 % <i>d,l</i> - or <i>l</i> -limonene, 4-6 % cadinene		Ditto
<i>Pinus sabiniana</i>	<i>n</i> -Heptane		A. W. Schorger (635)
<i>Pinus lambertiana</i>	70—75 % <i>d</i> - α -Pinene, 5 % β -pinene, 10-12 % sesquiterpene		Ditto
<i>Pinus ponderosa</i>	60 % <i>l</i> - β -Pinene, 20 % <i>l</i> -limonene, 10 % sesquiterpene, 5 % <i>l</i> - α -pinene	90 % Abietic acid	Ditto
<i>Pinus ponderosa scopulorum</i>	60-70 % <i>d</i> - α -Pinene, 5 % β -pinene, 20-25 % limonene		Ditto
<i>Pinus contorta</i> ...	<i>l</i> - β -Phellandrene (chiefly)		Ditto
<i>Pinus edulis</i> ...	70-75 % <i>d</i> - α -Pinene, 5 % β -pinene, 15-20 % <i>d</i> -cadinene		Ditto
<i>Pinus clausa</i> ...	75 % <i>l</i> - β -Pinene, 10 % <i>l</i> - α -pinene, 10 % <i>l</i> -camphene		A. W. Schorger (636)
<i>Pinus palustris</i> ..	64.3 % <i>d</i> - α -Pinene, 31.8 % β -pinene		G. Dupont and M. Barraud (637)
<i>Pinus caribea</i> ...	75.6 % α -Pinene, 21.2 % β -pinene		Ditto
<i>Pseudotsuga taxifolia</i>	<i>l</i> - α - and β -Pinenes and small amounts of <i>l</i> -limonene and <i>l</i> -terpineol		A. W. Schorger (638)
<i>Chamaecyparis lawsoniana</i>	45.7 % <i>d</i> - α -Pinene, 26 % <i>d</i> -borneol, 21 % cadinene, 3.9 % <i>l</i> -cadinol, 3.2 % <i>d</i> -limonene, aliphatic acid esters		F. H. Thurber and L. J. Roll; A. W. Schorger (639)

When wood is extracted with organic solvents, or pulped, preferably with alkali, *fats* are brought into solution, as well as resins. After the solvent has been evaporated the fats and resins are obtained as such; salting out the alkali solution after the pulping gives resins and fats in the form of alkali salts (soaps). The wood of certain trees is particularly rich in fat. One can therefore speak of "fatty trees" (*Tilia*, *Betula*, *Pinus silvestris*). O. Arrhenius (640) investigated the variations in the quantities of fat in various trees, and found that oak and maple have very low fat contents at all seasons, while alder, elm, ash, and mountain ash contain 0.5% of fat in summer, and 1% of fat in winter. Aspen, birch, spruce, and willow have fat contents of 0.75-2%, while linden and pine run as high as 6-7% in the winter. Spruce and pine show a sharp minimum in the fat content in June and July; the storing up of fat decreases as early as February or March, and the author thinks that this fact constitutes evidence that the storage of fat is not influenced by temperature, but is rather a periodic phenomenon. He also recommends felling the trees when

the fat content is at its maximum if the wood is to be pulped by alkaline procedures.

The investigations of A. Dahlén (641) have shown that linden contains an oil which is present to the extent of 7-8% of the dry weight. The oil content varies appreciably in different parts of the same tree, but is not dependent on the time of year, or on the age or manner of growth of the tree.

The fats of some conifers have been rather extensively studied. The resin soap which is obtained by salting out the black liquor from the production of soda pulp has often been used as a starting material in the investigations of pine and spruce fats. H. Bergström (642) found 53.1% of fatty acids and 49.9% of resin acids in the resin soap from pine. The fatty acids were a mixture of palmitic, oleic, and linolenic acids. H. Sandqvist (643) also found oleic and linolenic acids, but no palmitic acid. T. Hasselström (644) found large quantities of oleic acid, and also palmitic and linolenic acids, as well as certain indications of the presence of linoleic acid. The presence of two unknown acids could also be demonstrated. Stearic acid has shown to be present in the saturated fraction of fatty acids from tall oil (644 a, b). M. Dittmer (645) found only unsaturated fatty acids, including oleic, linoleic, and linolenic acids. W. Sander-mann (646) has demonstrated the presence of lignoceric acid ($C_{24}H_{48}O_2$).

Extraction of wood with acetone, ether, alcohol, benzene, chloroform, etc., causes the resins and fats to dissolve more or less completely. The following reports of C. G. Schwalbe and W. Schulz (647) indicate the manner in which the amount of dissolved material depends on the solvent used:

Kind of Wood	% Extracted with	
	Ether	Chloroform
Pine (Russian).....	5.2	2.6
Beech.....	0.9	2.5

A. B. Anderson (648) investigated the action of several solvents and solvent mixtures in the extraction of sawdust from ponderosa pine. Data both for the percentage of total extractives dissolved by the different solvents and for the selective action of these are given.

The amount of material extracted from wood depends very much on the storage of the wood before extraction, as E. Richter, (649), C. G. Schwalbe (647, 650), R. Sieber (651), and others have pointed out. The following figures serve to illustrate this point (647):

Length of Storage, Days	Solvent	Extract, % of Wood	% Resin in Extract	% Fat in Extract
85	Ether	6.9	67.2	32.8
127	Ether	2.5	87.9	12.1

Experiments of H. E. Wahlberg (652) have shown that drying the wood at 105° C also decreases the quantity of material which can be extracted with benzene.

The more finely the wood is divided, the more rapidly does the change in solubility take place. This change in solubility is evidently due to oxidation [Aschan (653)]. P. Klason and J. Köhler (654) found that the solubility of spruce resin in petroleum ether decreased on storage, and J. Nordenskjöld (655) found that the same thing was true of pine resin. R. Sieber (651) investigated this question in more detail. He reports the following results:

Resin	Ratio between Amounts Extractable with Ether and Alcohol	% of Ether-Extractable Material which is Soluble in Petroleum Ether
Fresh.....	17.7 : 1	94.5
Aged.....	4.7 : 1	13.4

Not all solvents are equally suited to the quantitative determination of resin. Certain solvents, particularly alcohols, dissolve some lignin in addition to the resin and fat, although the amount of lignin dissolved is usually small (Brauns' "native lignin", cf. p. 194). Resin obtained by extraction of spruce wood with ethyl alcohol contained appreciable amounts of lignin. As a matter of fact, A. Cleve-v. Euler (656) obtained widely varying amounts of extract (from 4.6 to 12.6%) when she extracted samples from various parts of the same trunk with alcohol-benzene mixtures. Part of this "alcohol resin" did not consist of resin and fat, but of lignin and carbohydrates (657). According to Klason, benzene alone can also dissolve a small amount of lignin.

Ether is an excellent solvent for unchanged resin and fat; it does not dissolve the other constituents of wood. It is therefore to be recommended for quantitative determinations. The oxidation products of resin have, however, only limited solubility in this solvent.

F. Barnes (658) gives the following figures for the amounts of material extracted first with ether and then with alcohol from the American soft-woods which are used in pulp-making.

Kind of Wood	Ether Extract %	Alcohol Extract %
White spruce.....	0.40	0.36
Black spruce.....	0.24	0.36
Balsam.....	0.85-1.20	1.35-1.71
Jack pine.....	2.37-3.24	0.77-1.71

Further data on the resin and fat contents of various kinds of wood may be found in section VI of this chapter (p. 350).

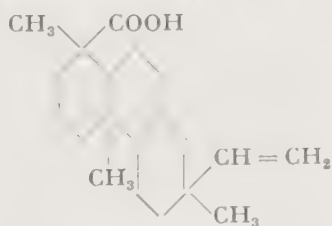
The substances included among the resins have been classified according to the following scheme by A. Tschirch (659):

1. Resin acids (mostly free, i.e., not esterified).
2. Resin alcohols: a) resin alcohols without tanning properties, and b) resinotannin alcohols with tanning properties. These alcohols are partially esterified with resin acids or other acids.
3. Resenes. Characterized by their insolubility in alkali.

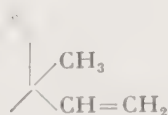
Tschirch attempted to separate the constituents of resin by extracting the ether solution of the resin first with ammonium carbonate, then with soda, and finally with dilute potassium hydroxide. This caused the acids to dissolve first, and the very weakly acid constituents to dissolve last. That part of the neutral fraction which consisted of esters (2) could then be determined by saponification. The remainder (3) was not saponifiable.

Resin acids, which make up almost all of the resin of softwoods, are frequently mixed with other acids. The chemical properties of softwood resin acids with the empirical formula $C_{20}H_{30}O_2$ have been studied particularly thoroughly.

Among the native resin acids the dextrorotatory dextropimaric acid and the levorotatory levopimaric acid deserve special mention. They are not, as the name would indicate, optical isomers. Both occur in various balsams, in that from *Pinus silvestris*, for example. The dextropimaric acid is stable at high temperatures and in the presence of acids. From the oleoresin of *Pinus palustris*, the stereoisomeric *iso*-dextropimaric acid has been isolated by G. C. Harris and T. F. Sanderson (659 a). The following structures have been established for these two acids (660, 659a):

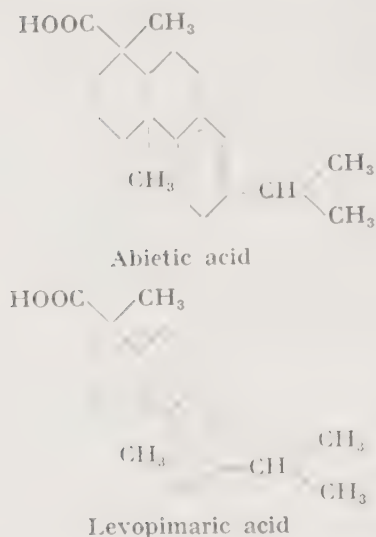


Dextropimaric acid



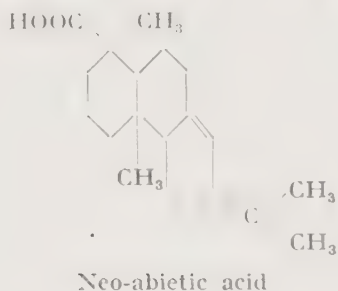
Isodextropimaric acid

The levopimaric acid is on the other hand very unstable, and is easily isomerized by acids or by heat. One of the stable isomers is abietic acid, which occurs in colophony. Levopimaric acid reacts readily with maleic anhydride, and therefore appears to have two conjugated double bonds. Abietic acid also yields the same maleic anhydride addition product, but with much more difficulty. The conversion of levopimaric acid to abietic acid is the result of a change in the position of the double bonds.



In these formulas only the position of the double bonds is still uncertain (661).

A further acid of the abietic-type, neo-abietic acid, has recently been isolated from the oleoresin and rosin of *Pinus palustris* (661a).



Fundamental to the elucidation of these structures was K. A. Vesterberg's discovery (662) that dehydrogenation of abietic acid led to the formation of retene, 1-methyl-7-isopropylphenanthrene.

Abietic acid is not the end product of the rearrangement of levopimaric acid. Heating causes a disproportionation which results in the formation of dehydroabietic acid (with an aromatic ring) and di- and tetrahydroabietic acids. Substances with lactone rings are also formed. Such mixtures probably occur in tall oil (663).

Some further resin acids have been found in different resins. Kauri resin and Manila copal contain agathenedicarboxylic acid (664); the resin of *Podocarpus ferrugineus* contains ferruginol (665), which is a phenol related to dehydroabietic acid.

Among the *resin alcohols* without tanning properties, the amyriols of elemi resin and the betulin of birch bark should be mentioned. Like

abietic acid, they are terpene-like substances. Resins also contain mixtures of *sterols*, like β -sitosterol and stigmasterol (dihydrositosterol), which can be obtained from tall oil (666) and other sources. II. Hibbert and S. B. Phillips (644 a) found the ether extract of Jack pine to contain 18% phytosterols. According to E. F. Kurth (644 b), 30-60% phytosterols were present in the unsaponifiables from sapwood of Longleaf and Shortleaf pine, but only 6% in the unsaponifiables from heartwood.

A sitosterol as well as a dihydrositosterol have also been found in the extractives from pine bark [K. Pajari (667)]. From the unsaponifiable part of the ether extract from black spruce, L. E. Wise and S. T. Moore (668) have isolated a sterol, probably 22,23-dihydrostigmasterol.

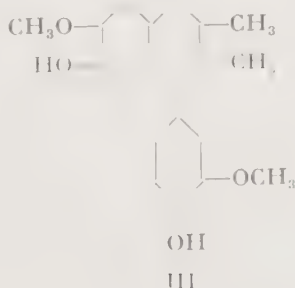
Other resin alcohols are phenolic. Among these latter a group of *dimeric phenylpropanes* deserves special mention, because they are interesting from a biogenetic point of view. As already mentioned (p. 322), it has been supposed, that certain members of this group represent intermediate stages in the formation of lignin.

The investigation of the structure of these substances has shown that they are either diarylbutanes (I) or phenylnaphthalenes (II) (669). At the suggestion of R. D. Haworth (670) the entire group has been given the name of "*lignans*."

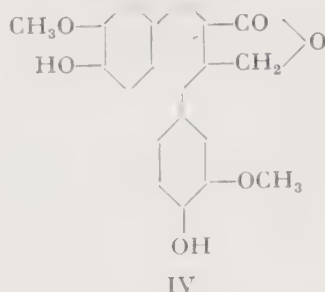


Certain phenylpropanes are easily dimerized *in vitro*, and it is very probable that the lignanes in plant cells are formed by the enzymatic coupling of phenylpropane derivatives. They often occur in nature in company with simple phenylpropane derivatives.

The simplest of these substances is guaiaretic acid (III) which occurs in the heartwood of *Guaiacum officinale* (671):

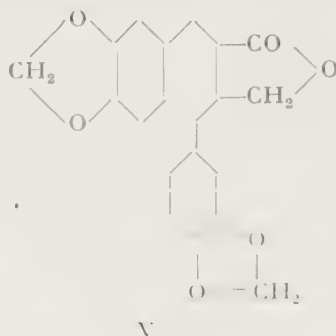


The matairesinol of the heartwood of *Podocarpus spicatus* is a lactone (IV) (672):



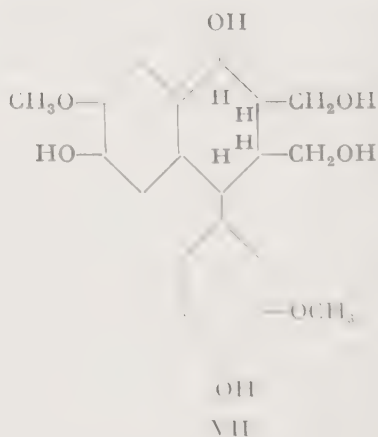
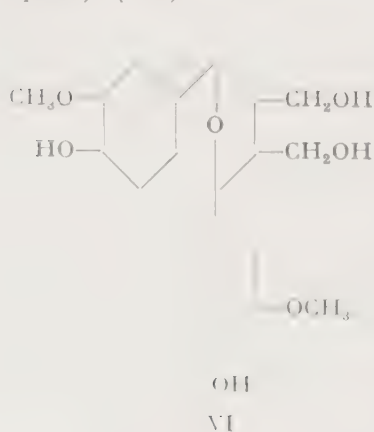
It occurs in this wood along with conidendrin (X) (p. 342), to which it is genetically very closely related.

Hinokinin (V) is obtained from the heartwood of *Chamaecyparis obtus cupressus* (673):



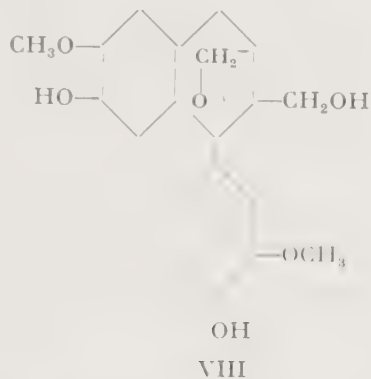
The steric configuration is the same as that of matairesinol. This was proved by splitting off the methylene groups and subsequent methylating the liberated phenolic hydroxyls; the dimethyl ether of matairesinol was obtained.

Olivil (VI) occurs in large quantities in the resin of the olive tree (*Olea europaea*) (674):



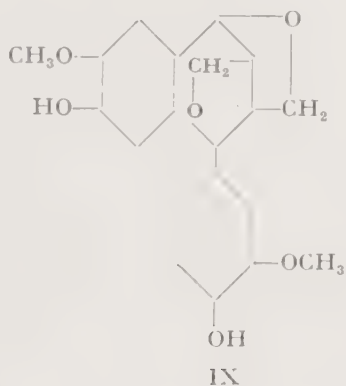
It is easily rearranged to isoolivil (VII) by acids. Isoolivil occurs naturally in the wood of *Olea Cunninghamii* (675); it is closely related to conidendrin.

The resinous exudates which cover over injuries in the larch (*Larix decidua*) contain lariciresinol (VIII) (676):



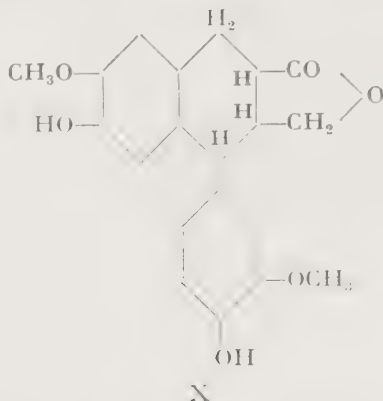
Like olivil, it is easily isomerized by acids. Isolariciresinol is thus formed; the dimethyl ether of the latter is dehydrogenated to conidendrin dimethyl ether by sodium hypobromite. This proves the steric similarity between lariciresinol and conidendrin.

The resinous exudates which cover over injuries to *Picea excelsa* and *Engelmannii f. glauca*, *Pinus nigra*, *P. ponderosa scopularum*, and *P. silvestris*, contain pinoresinol (IX) (677):



The eudesmin (678) of the resinous exudate of various eucalyptus trees (e.g. *Eucalyptus hemiphloia*) has been found to be the optical isomer of pinoresinol dimethyl ether (678 a). Methylenedioxy analogs of pinoresinol and of eudesmin occur in various herbs. The gmelinol (679) from the wood of *Gmelinia Leichardtii* appears to be closely allied to pinoresinol dimethyl ether, probably being a hydroxy derivative (680).

Conidendrin (sulfite waste liquor lactone, cf. p. 322) (X) occurs in various conifers. Its presence in the resin of *Podocarpus spicatus* has already been mentioned.



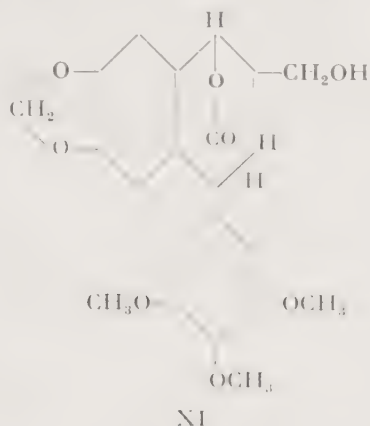
By sulfite digestion of the wood and examination of the waste liquors H. Erdtman (681) has investigated the occurrence of conidendrin in some genera of the conifer group. Seven of the fourteen *Picea* species investigated (of about 35 known) and four of the four *Tsuga* species (of 11 known), but only one of the seven *Abies* species (about 40 known) contained conidendrin. No conidendrin could be found in any species examined belonging to the genera *Pinus*, *Pseudotsuga* and *Larix*. Since conidendrin also could be isolated directly from spruce wood, it appears to be present as such in the wood and is not formed from an unknown precursor during sulfite cooking. Like the phenolic stilbenes of pine heart wood (see p. 343), conidendrin is obviously deposited inside of membranes (682), which are insoluble in ether but soluble in acetone. Conidendrin, although ether-soluble in the isolated state, can therefore not be extracted from spruce wood by ether, but is readily extracted by acetone.

F. E. Brauns (683) has isolated conidendrin also from the wood of Western hemlock (*Tsuga heterophylla*), and J. A. Pearl (684) recovered it from a sulfite waste liquor of the same wood species.

A simple method of precipitating the conidendrin from sulfite waste liquor has been found by H. B. Lackey, M. W. Moyer, and W. M. Hearon (684 a). It consists of mixing the waste liquor with small amounts of organic solvents such as trichlorethylene (0.25-10% by volume), and allowing the mixture to stand. Yields up to 0.66 g. conidendrin per liter waste liquor from Western hemlock have thus been obtained.

Conidendrin may have future industrial interest since W. G. Bickford and co-workers (684 b) have found that norconidendrin, which is obtained by demethylation of conidendrin with hydrogen bromide or pyridine hydrochloride (684 c), is an antioxidant for fats, oils and paraffin.

Finally, podophyllotoxin (XI) occurs in the roots of certain berberidaceae, like *Podophyllum peltatum* (685). It is therefore particularly interesting, since, like the lignin of angiosperms, it contains not only pyrocatechol groups, but also pyrogallol groups:

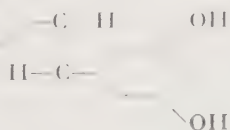


The ultraviolet absorption of several lignans has been investigated by G. Aulin-Erdtman and H. Erdtman (686). H. Erdtman (687) and R. D. Haworth (688) have published reviews of the chemistry of these natural products.

Resenes certainly occur quite often in the resins of certain trees, but only in relatively small quantities. The chemical nature of these compounds is not known in any detail.

B. PHENOLS, TANNINS. COLORING MATTER AND NITROGEN-CONTAINING SUBSTANCES

It has been demonstrated by H. Erdtman (689) that the heartwood of pine contains phenolic stilbene derivatives which make this wood resistant to the attack of fungi and of insects. They also make it impossible to pulp the heartwood by the usual sulfite procedure (cf. p. 444). Pinosylvin (*trans*-3,5-dihydroxystilbene) and its monomethyl ether have been isolated from the heartwood of the common (European) pine, *Pinus silvestris*.

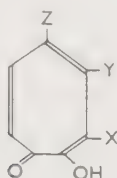


Other pines contain the dimethyl ether, too. Pinosylvin derivatives seem to be characteristic of the genus *Pinus*; pinosylvin and pinosylvin

monomethyl ether have been found by H. Erdtman (690) in all the kinds of pines which have been investigated so far; 25-35% of the total amount of pinosylvin and pinosylvin monomethyl ether consisted of pinosylvin. The dark red color, which appears, when pine heartwood is treated with bis-diazotized benzidine (691) is due to the presence of pinosylvin and its monomethyl ether. Since the pinosylvins are stilbene derivatives, they are characterized by a strong fluorescence. The constitution of pinosylvin was established both by degradation (689) and by synthesis (692).

R. F. B. Cox (693) found 3,5-dimethoxystilbene in the unsaponifiable part of a resin extracted with benzene from spruce stumps.

The presence of phenolic substances in the heartwood of Western red cedar (*Thuja plicata*) has been demonstrated by A. B. Anderson and E. C. Sherrard (694). H. Erdtman and J. Gripenberg (695) have elucidated the structure of these substances and called them α -, β -, and γ -thujaplicin; they are the three possible isopropyl derivatives of a cycloheptatrienolone (= tropolone):



α -Thujaplicin: X = $(\text{CH}_3)_2\text{CH}-$; Y = Z = H

β -Thujaplicin: Y = $(\text{CH}_3)_2\text{CH}-$; X = Z = H

γ -Thujaplicin: Z = $(\text{CH}_3)_2\text{CH}-$; X = Y = H

The *tannins* are important constituents of wood. These substances are usually localized in the bark of the wood. Spruce bark contains 8-9% of tannins, and pine bark, 4-8%. P. Klason and T. Edlund (696) found 11.4% in spruce bark and 10.2% in German oak. The bark of willow contains 12-13% of tannins (697). The wood itself is much poorer in tannins. The wood rays are relatively rich in these substances. Especially high in tannin content is quebracho wood, with approximately 16% of tannins. Chestnut wood has about 8%. Oak wood also contains tannins; this is the reason why it is resistant to both wet and dry rot.

K. H. Benson and F. M. Jones (698) investigated the tannin content of various American woods, with the following results

Type of Wood	% of Tannin in	
	Bark	Wood
Western larch	10.6	6.7
Western yellow pine . . .	10.9	8.9
Western hemlock	10.9	1.0
Dogwood	1.7	1.3
Cottonwood	4.7	1.8
Alder	3.3	0.7

These figures may be supplemented with those for the tannin content

of redwood, reported by C. C. Scalione and D. R. Merrill (699). [These values may be too high. Cf. J. A. Wilson and E. J. Kern (700).]

Tannin Content in %

	Bark	Heartwood	Sapwood
Redwood.....	0.86	12.2	1.15

Of more recent investigations the following values of L. V. Forman and D. D. Niemeyer (701) may be mentioned:

Kind of Wood	% of Tannin in	
	Bark	Wood
Buttonbush (<i>Celphalanthus occidentalis</i>).....	4.2	0
Pin oak (<i>Quercus nigra</i>).....	4.3	0
Longleaf pine (<i>Pinus palustris</i>).....	5.0	0
Yaupon (<i>Ilex vomitoria</i>).....	7.8	0
Wild olive tree (<i>Halesia carolina</i>).....	11.5	0
Red mangrove (<i>Rhizophora mangle</i>).....	24.2	0
Black oak (<i>Quercus velutina</i>).....	8.4	trace
White oak (<i>Quercus alba</i>).....	7.9	2.7
Darling plum (<i>Reynosia septentrionalis</i>).....	8.2	6.9
Coastal Chinquapin (<i>Castanea Ashei</i>).....	12.0	12.3

Two classes of tannins are known. One class is hydrolyzable with acids to sugars, gallic and ellagic acids ("hydrolyzable tannins"). The other class, also called phlobatannins, is composed of low-molecular or polymerized catechins ("non-hydrolyzable tannins"). The following table gives the composition of the tannins of some woods and barks, used in the preparation of commercial tannins (702, 702 a):

Kind of Wood or Bark	Tannin
Chestnut	Chestnut gallic acid
	Ellagic acid
	Gallic acid
	Quercetin
Oak	Quercitannic acid
	Ellagic acid
<i>Acacia catechu</i>	Catechin
	Epicatechin
Quebracho	Quebracho catechin
Wattle	Catechin tannins
Spruce bark	Probably catechin tannins
Hemlock bark	Catechin tannins

A number of tropical woods contain *dyes*. Some of these have attained great practical importance. Examples of colored woods are: logwood (*Hematoxylon campecheanum*) with the chromogen hematoxylin, Pernambucowood or Brazilwood (*Caesalpinia echinata* Lam.) with the chromogen brazilin, other woods of the *Caesalpinia* type, which are grouped under the name of West-Indian redwoods, sandlewood (*Pterocarpus santalinus*, L.) with the coloring matter santalin, teakwood, with the dye tec-

toquinone, Bignoniaceae, e. g., lapachowood with lapachol, amaranthwood with the chromogen phenin and the dyestuff phenizein, jackwood (*Artocarpus integrifolia*) with the chromogen cyanomac lurin and the true yellow-wood (*Chlorophora tinctoria*) with the dyestuffs morin and mac lurin, quebrachowood and fustic wood with the dyestuff fisetin, etc.

Logwood is the most important of these colored woods. Hematoxylin is extracted from the finely divided wood (extract of logwood). The colorless hematoxylin is oxidized to hematein. This oxidation with chromic acid or with ferric salts, which simultaneously act as mordants, takes place when wool or cotton is dyed black with extract of logwood. Brazilin forms colorless crystals, which are converted to the dye brazilein by oxidation. Santalin is a dye which colors wool and cotton Bordeaux red in the presence of alumina or other mordants. Morin with a chromium mordant colors wool a brown-yellow.

The chemical constitution of the chromogens and dyestuffs of the colored woods mentioned above has been largely worked out. This subject can not be discussed in detail here.

A number of flavones, like chrysin and tectochrysin as well as flavanones, like pinocembrin, pinobanksin, and pinostrobin, have been isolated by H. Erdtman (703) from the heartwood of various *Pinus* species. G. Lindstedt (703 a) has thoroughly studied the occurrence of these phenolic constituents, as well as pinosylvin and its methyl ether, in different pine species, and has developed a paperchromatographic method for their separation and identification. Taxifolin, a 3,5,7,3',4'-penta-hydroxyflavanone, has been isolated by I. C. Pew (704) from the wood of Douglas fir in yields of about 2 per cent. Similar to the phenolic stilbene derivatives in pine heart wood (cf. Chapter V, page 444), this flavanone inhibits the sulfite pulping of Douglas fir heartwood.

In this connection the frequent occurrence of the so-called leucoanthocyanins in many woods should be noted. These substances are regarded as precursors of the flower pigments, the anthocyanins. They are converted by oxidizing agents like oxygen, in the presence of acids or of light, into anthocyanins or their aglucons, the anthocyanidins (e.g., cyanidin). The most-thoroughly investigated of these materials is peltogynol, from the heartwood of *Peltogyne porphyrocardia* (705).

The nitrogen content of various woods is small, and varies between 0.1 and 0.5%. C. G. Schwalbe and E. Becker (706) obtained the following values when they analyzed the woods mentioned below for nitrogen. They assumed that the nitrogen was derived exclusively from proteins, and calculated the approximate protein content of the woods by multiplying the nitrogen values by 6.25.

	Spruce	Pine	Beech	Birch	Poplar
Nitrogen %.....	0.11	0.13	0.17	0.12	0.10
Protein %.....	0.69	0.80	1.05	0.74	0.63

R. Hartig (707) established the interesting fact that the nitrogen content of beech wood varies with the season, and that it is connected with the formation of fruit. It therefore varies between 0.01 and 0.1%. When the formation of fruit is at its height, the nitrogen content is at its minimum.

The assumption that the nitrogen is derived chiefly from proteins is a very plausible one, but has not yet been demonstrated experimentally. It was formerly widely believed that the proteins occur in the *cell wall*. W. Hoffmeister (708) demonstrated, however, that the young cell wall is free of substances containing nitrogen. The proteins are therefore present only in the cells containing protoplasm.

Alkaloids can also occur in wood. T. Molle (709) found that wood of the roots of *Datura* contains alkaloids when the roots are young. Berberine has also been found in the wood of certain barberries. A number of tropical woods contain varying amounts of alkaloids; certain types of *Strychnos* contain 1-2% of strychnine and brucine, for example.

A review of the extractives of American pulp woods covering the literature from 1932 to 1945, has been given by L. H. Isenberg, M. A. Buchanan and L. E. Wise (710). H. Erdtman (710 a) has published a review of the extractives from the heartwood of conifers.

C. INORGANIC COMPONENTS

The ash content of wood is quite variable, not only from one type of wood to another, but also for the same type of wood. The ash content varies with the place where the wood is grown, the growing conditions, and the season of the year. The content of minerals even varies from one part of the same tree to another. The ash content of heartwood is usually less than that of the sapwood, and that of the trunk is less than that of the branches. These rules are subject to certain exceptions.

H. Zimmermann (711) determined, for example, the ash content of different concentric layers in the trunk of a 94-year-old beech tree. His results were as follows:

Annual Ring	Ash Content, %
1-15 (Heartwood).....	1.162
15-25.....	0.825
25-35.....	0.645
35-45.....	0.612
45-60.....	0.555
60-83.....	0.458
83-94 (Sapwood).....	0.205

The ash in the sapwood is here less than in the heartwood; this is attributed to the deposition of calcium compounds in the heartwood.

The following data of H. Schroeder (712) on the ash content of various portions of a single tree are also of interest:

	Ash Content, %	
	Spruce	Birch
Trunk.....	0.169	0.160
Topmost part of trunk.....	0.26	—
Branches.....	0.32	0.64

Schroeder also investigated the variation in ash content with the time of year; the following figures for spruce demonstrate that small variations do occur. These variations may be explained on the basis of the variation in the amount of dissolved minerals carried through the stem at various times of the year.

	% of Ash in Spruce Wood			
	April	August	November	February
Outer wood.....	0.226	0.229	0.252	0.199
Inner wood.....	0.201	0.224	0.236	0.189
Total (for all wood).....	0.213	0.226	0.243	0.194

Only small amounts of the mineral substances can be dissolved by leeching out the wood with water. These substances are therefore firmly bound, either chemically or mechanically. H. Schroeder (712) was able to decrease the ash content of spruce from 0.232% to 0.183% by extraction with water. Most of the mineral constituents of wood can be dissolved by treatment with dilute hydrochloric acid (713).

The chemical composition of the ash is quite inconstant, as may be seen from the following figures of W. Daube (714):

Kind of Wood	Ash, %	Parts per 10,000 (hundredths of a per cent)							
		K ₂ O	P ₂ O ₅	CaO	MgO	Fe ₂ O ₃	SO ₃	SiO ₂	Na ₂ O
Larch									
Sapwood.....	0.22	5.32	1.28	6.84	3.33	1.10	1.27	1.08	0.90
Heartwood.....	0.12	2.97	0.15	4.03	1.94	0.93	0.55	0.25	0.59
Pine									
Sapwood.....	0.19	5.40	1.37	5.25	2.09	1.19	0.98	0.39	0.87
Heartwood.....	0.15	2.30	0.13	6.28	2.41	0.83	0.68	0.52	0.47
Spruce									
Sapwood.....	0.26	9.80	2.87	5.54	1.46	1.54	1.11	0.72	0.38
Heartwood.....	0.20	5.93	0.20	7.36	1.96	1.71	0.86	0.20	0.65
Oak									
Sapwood.....	0.42	19.56	5.22	6.93	2.63	1.46	2.90	0.56	1.13
Heartwood.....	0.16	6.71	0.43	4.08	0.44	0.51	1.98	0.88	0.24
Beech									
Sapwood.....	0.47	19.24	2.15	12.56	6.77	1.65	1.93	0.59	0.53
Heartwood.....	0.40	15.47	0.60	13.33	5.11	0.82	1.55	0.82	0.17

The potassium content of the sapwood is evidently higher than that of the heartwood. According to R. Weber (715), this relationship is reversed in the case of beech. The potassium content of the pure ash varies with the season of the year, as is shown by the following figures of Schroeder (712):

	K ₂ O in % of the Pure Ash of Spruce Wood			
	April	August	November	February
Outer wood.....	23.36	17.81	21.22	22.12
Inner wood.....	18.25	17.27	15.25	18.20

The fact that manganese is present is also interesting. In beech wood the manganese (calculated as MnO) constitutes 1-2% of the total ash, and in spruce it is approximately 5%. Larch wood is reported not to contain manganese.

For the presence of other trace elements in wood see ref. 716.

D. OTHER WOOD COMPONENTS

The occurrence of *acetyl groups* in wood has already been discussed in another connection. The presence of these groups is demonstrated by the fact that alkaline or acid saponification yields considerable amounts of acetic acid. It was long thought that these acetyl groups were bound to the lignin (717). W. H. Dore (718), however, believed that it was possible that a part of the acetyl groups were bound to the carbohydrates. This was later proved by E. Schmidt and his co-workers. They found that all of the acetyl groups are attached to the "skeletal substance" of beech wood which remains after all of the lignin has been removed. It was found indeed, that only the pentose fraction of the wood had any acetyl attached. P. B. Sarkar (719) asserts that the acetic acid obtained from *jute* is not derived from the cellulose or the wood polyoses, but rather from the pectins.

The results of Schmidt were later confirmed by G. J. Ritter (720) and his co-workers. They extended this investigation to American spruce, maple, and oak. The investigations of Y. C. Tang (721) and his co-workers also appear to indicate that all the acetyl is present in the "skeletal substance."

The acetyl groups are determined by splitting them off with acid or alkali; comparative experiments have been carried out by F. W. Klingstedt (722). The method of K. Freudenberg (723) in which the material is treated with an alcoholic solution of *p*-toluenesulfonic acid appears to

give reliable results. The procedure of P. Klason in which the wood is digested with saturated lime water at 60°C is even simpler (724).

Formic acid is also formed when wood is hydrolyzed.

The manner in which this acid arises has not yet been explained. It is natural to assume that it is formed by saponification of formyl groups. Since as much formic acid is obtained from the "skeletal substance" as from the wood itself, it must be concluded that the lignin does not give rise to any formic acid (720, 722).

The acetyl and formyl contents of the same kind of wood are not constant. The variations are shown by the following figures, obtained for Swedish spruce and pine (725):

S p r u c e				P i n e			
Sample No.	Taken Within (A) or Below (B) the Crown	Acetic Acid %	Formic Acid %	Sample No.	Taken Within (A) or Below (B) the Crown	Acetic Acid %	Formic Acid %
1	B	1.90	0.26	1	B	1.83	0.17
2	A	1.91	0.22	2	A	1.78	0.25
3	B	1.88	0.15	3	B	1.57	0.36
4	A	2.08	0.19	4	A	1.56	0.29
5	B	1.97	0.20	5	B	1.70	0.25
6	A	2.02	0.24	6	B	1.48	0.25
9	B	1.86	0.25	7	B	1.82	0.22
10	A	2.04	0.25	8	B	1.36	0.27
11	B	1.65	0.29	13	B	1.67	0.33
12	A	1.77	0.28	14	A	1.91	0.20
13	B	1.68	0.27	21	B	1.42	0.29
14	A	1.73	0.29	22	A	1.69	0.22
15	B	1.96	0.32	23	B	1.34	0.24
16	A	2.15	0.32	24	A	1.29	0.36

VI. Analyses of Wood

Comprehensive studies of the chemical compositions of various woods have been made at various times. P. Klason (726) was probably the first to attempt to report the composition of spruce wood. He found the following values:

	%
Cellulose.....	53.0
Other carbohydrates.....	14.0
Lignin.....	29.0
Proteins.....	0.7
Resin and fat.....	3.3
	100.0

Comprehensive analyses of German woods were made later, especially by J. König (727) and by C. G. Schwalbe and his co-workers.

Per Cent of the Weight of the Wood

Kind of Wood	Protein (N×6.25)	Resin (Alcohol-Benzene Extract)	Ash	Total Pentosan	Hemicellulose ¹			Cellulose, (by Difference)	
					Hexosan	Pentosan	Lignin	Including Pentosan	Pentosan Free
Fir.....	1.21	2.83	1.10	11.48	13.58	8.67	29.17	43.44	40.62
Fir.....	1.21	1.71	0.42	11.63	13.00	9.74	27.98	45.95	44.06
Pine.....	1.27	3.17	0.53	10.80	12.78	8.70	29.52	44.01	41.93
Birch.....	1.29	2.47	0.68	25.86	4.61	23.20	28.27	44.53	41.85
Birch.....	2.29	1.88	0.46	24.01	5.00	21.48	26.38	42.50	39.97
Poplar.....	1.39	2.66	0.84	22.71	2.60	15.36	22.45	54.71	47.36
Poplar.....	1.14	2.32	1.21	21.88	3.43	15.10	20.75	56.06	49.27
Beech.....	1.58	0.70	0.96	24.30	4.36	17.79	22.69	51.93	45.41
Ash.....	1.30	2.24	0.83	23.68	5.70	19.29	26.01	44.64	40.24
Willow.....	1.17	2.04	0.83	23.31	5.05	16.75	24.70	49.46	42.91
Alder.....	1.89	2.83	0.49	22.94	3.65	15.90	24.57	50.69	43.64

¹ Determined by hydrolysis with acid at various pressures.

C. G. Schwalbe and E. Becker (728) determined the composition of several German woods by a method worked out by Schwalbe (729). The wood was taken from trees 60 to 80 years old.

Per Cent of the Water-Free Material

Constituent	Spruce (<i>Picea Excelsa</i>)	Pine (<i>Pinus Silvestris</i>)	Beech (<i>Fagus Silvatica</i>)	Birch (<i>Betula Verrucosa</i>)	Aspen (<i>Populus Tremula</i>)
Ash.....	0.77	0.39	1.17	0.39	0.32
Resin, wax, and fat					
a. Ether extract.....	0.78	1.92	0.31	0.71	1.08
b. Alcohol extract.....	1.52	1.53	1.74	1.09	2.08
c. Sum of a and b.....	2.30	3.45	2.05	1.80	3.16
d. Alcohol-benzene extract....	2.34	3.32	1.20	1.68	2.87
Methyl number (CH ₃).....	2.36	2.20	2.96	2.77	2.57
Methyl alcohol.....	0.122	0.111	0.175	0.161	0.182
Pectin, calc.....	1.22	1.11	1.75	1.61	1.82
Acetic acid (volatile acids, Schorger)	1.44	1.40	2.34	4.65	4.17
Nitrogen.....	0.11	0.13	0.17	0.12	0.10
Protein (N × 6.25).....	0.69	0.80	1.05	0.74	0.63
Pentosan.....	11.30	11.02	24.86	27.07	23.75
Methylpentosan.....	3.00	2.23	1.02	0.84	0.72
Cellulose.....	63.95	60.54	67.09	64.16	62.89
Cellulose, free of pentosan.....	57.84	54.25	53.46	45.30	47.11
Lignin.....	28.29	26.35	22.46	19.56	18.24

C. G. Schwalbe and E. Becker (730) also investigated the changes in the composition of wood brought about by aging. The wood investigated was alder (*Alnus glutinosa*).

It was found that the heartwood contained about 1% more lignin than did the sapwood. More acetic acid was split from the younger wood than from the older, when a Schorger-hydrolysis (712) was carried out. No other differences worthy of note were observed.

The chemical compositions of the spring- and summerwoods of spruce were investigated by E. Hägglund and T. Johnson (731), with the following results:

	Springwood	Summerwood
Water content, % of wet wood	10.41	10.39
Ash content, % of dry wood	0.33	0.29
Ether extract.....	0.76	0.62
Lignin (with strong hydrochloric acid).....	28.45	28.45
Methoxyl.....	4.66	4.92
Pentosan.....	7.58	6.77

Chemical analyses of many American woods have been made by A. W. Schorger (732), S. A. Mahood and D. E. Cable (733), and G. J. Ritter and L. C. Fleck (734). The results are summarized in the table on p. 353. Acetic acid was determined according to Schorger, pentosan and methylpentosan, according to Tollens, and cellulose, according to Cross. Lignin was determined after digesting with 72% sulfuric acid, and the other substances in the usual way. The values given are averages of three or four analyses.

The chemical composition of the wood varies from the heartwood to the sapwood, and from the springwood to the summerwood, as is shown in the tables on pp. 354 and 355. These analyses were carried out by G. J. Ritter and L. C. Fleck (735). [W. I. Scharkow and W. Muromzewa (736) have made the surprising report that Russian pine contains no less than 4.15% of araban and 0.73% of methylpentosan. They found as much as 7.71% of araban in birch wood, but no methylpentosan.]

In connection with the last table it should be noted that the lignin content of the springwood is greater than that of the summerwood. This is especially noticeable in the hardwoods. Ritter and Fleck suppose that this is due to the fact that the middle lamella, which is rich in lignin, makes up a larger portion of the springwood than of the summerwood. The analyses of E. Hägglund and T. Johnson, mentioned above, do not show any difference in the lignin contents of spring- and summerwood of spruce. From the methoxyl contents one might conclude, indeed, that the summerwood had more lignin than the springwood.

The composition of the wood is not the same at all points in the tree. The following tables give figures for the trunk.

Grams per 100 g. Dry Weight

Kind of Wood	Ash	Soluble in				Acetic Acid	Methoxyl	Pentosan	Methyl-pentosan	Cellulose	Lignin	In the Cellulose, %				Author
		Cold Water	Hot Water	Ether	1% NaOH							Pen-tosan	Me-thyl-pen-tosan	α -Cellu-lose	β -Cellu-lose	
Longleaf pine	0.37	6.20	7.15	6.32	22.36	0.76	5.05	7.46	3.60	58.48	—	7.71	1.16	—	—	Schorger
Douglas fir . .	0.38	3.54	6.50	1.02	16.11	1.04	4.95	6.02	4.41	61.47	—	5.34	1.20	—	—	"
Western larch	0.23	10.61	12.59	0.81	22.14	0.71	5.03	10.80	2.81	57.80	—	8.94	1.19	—	—	"
White spruce	0.31	1.12	2.14	1.36	11.57	1.59	5.30	10.39	3.55	61.85	—	9.63	0.72	—	—	"
Western white pine .	0.20	3.16	4.49	4.26	14.78	1.03	4.56	6.97	3.22	59.71	26.44	5.33	1.95	64.61	16.32	Mahood and Cable
Western yellow pine . .	0.46	4.09	5.05	8.52	20.30	1.09	4.49	7.35	1.62	57.41	26.65	6.82	1.98	62.10	10.56	Ritter and Fleck
Yellow cedar .	0.43	2.47	3.11	2.55	13.41	1.59	5.25	7.87	3.42	53.86	31.32	7.30	1.78	62.68	11.06	"
Incense cedar	0.34	3.64	5.38	4.31	17.69	0.91	6.24	10.65	1.35	41.60	37.68	9.08	1.99	46.92	11.67	"
Redwood . . .	0.21	7.36	9.86	1.07	20.00	1.08	5.21	7.80	2.75	48.45	34.21	7.40	2.09	78.81	2.95	"
Tanbark oak	0.83	4.10	5.60	0.80	23.96	5.23	5.74	19.59	—	58.03	24.85	22.82	—	56.77	19.92	"
Mesquite . . .	0.54	12.62	15.09	2.30	28.52	2.03	5.55	13.96	0.70	45.48	30.47	17.75	0.81	76.48	2.35	"
Balsa	2.12	1.77	2.79	1.23	20.37	5.80	5.68	17.65	0.86	54.15	26.50	19.99	1.35	75.64	0.27	"
Hickory	0.69	4.78	5.57	0.63	19.04	2.51	5.63	18.82	0.80	56.22	23.44	21.89	1.41	76.32	2.82	"
Passwood . . .	0.86	2.12	4.07	1.96	23.76	5.79	6.00	19.93	3.73	61.24	—	24.28	1.54	—	—	Schorger
Yellow birch	0.52	2.67	3.97	0.60	19.85	4.30	6.07	24.63	2.69	61.31	—	28.30	1.16	—	—	"
Sugar maple .	0.44	2.65	4.36	0.25	17.64	4.46	7.25	21.71	2.39	60.78	—	24.48	0.96	—	—	"
Eucalyptus . .	0.24	4.67	6.98	0.56	18.57	1.85	6.73	20.09	2.33	57.62	25.07	20.96	2.46	68.86	0.70	Mahood and Cable

Grams per 100 g. Dry Weight

Constituent	Incense Cedar		White Cedar		Yellow Cedar		White Pine		Bald Cypress		White Oak		Yellow Birch		Pignut Hickory		Yellow Poplar		White Ash	
	II	S	II	S	II	S	II	S	II	S	II	S	II	S	II	S	II	S	II	S
Ash.....	0.30	0.47	0.27	0.48	0.18	0.28	0.42	0.23	0.95	0.86	0.43	0.57	0.40	0.26	0.45	0.40	0.33	0.36	0.32	0.57
Soluble																				
	4.72	1.92	2.80	3.02	2.88	2.13	5.97	3.55	3.27	1.76	7.33	2.25	4.16	1.05	2.07	4.91	1.45	1.45	2.12	5.25
	7.08	2.97	4.01	3.96	4.12	3.41	7.68	5.15	3.49	2.30	10.15	4.11	5.69	1.98	2.95	6.45	2.89	2.51	4.46	7.02
	4.78	0.67	1.87	1.41	1.32	1.00	3.62	5.46	7.93	2.80	0.71	0.46	0.81	0.48	0.36	0.29	0.58	0.13	0.46	0.88
1% NaOH.....	19.99	11.16	14.14	12.71	12.77	11.72	19.15	17.16	13.56	10.63	25.81	21.11	20.51	16.77	15.10	19.11	17.57	16.91	18.97	21.93
Acetic acid (Schorger)...																				
	0.68	1.33	0.74	1.11	1.53	2.05	1.43	1.68	0.29	0.65	2.59	3.44	1.78	2.34	3.08	3.58	2.73	3.33	2.66	3.70
	6.21	5.95	5.09	5.23	4.81	4.40	4.60	4.16	4.07	4.99	6.18	5.95	5.46	5.66	5.79	5.56	6.03	5.89	5.20	5.66
	12.04	12.08	10.36	10.82	8.69	8.17	8.56	9.31	7.88	9.23	21.82	23.25	20.37	21.36	18.64	18.18	19.08	18.82	19.87	20.16
Methyl- pentosan....																				
	0.56	0.45	1.56	1.16	1.85	1.75	1.00	2.14	3.36	3.34	1.57	0.90	1.39	1.66	1.02	1.11	1.13	1.22	2.46	2.63
	44.53	49.09	54.42	55.02	56.08	58.12	50.23	54.25	49.18	50.94	48.68	49.53	56.88	58.91	58.81	56.08	59.47	58.02	53.40	49.72
	33.67	34.73	32.42	32.11	28.73	29.03	26.14	26.51	32.27	35.31	32.74	32.34	24.62	24.69	22.85	21.87	23.69	23.86	28.38	27.39
In Cellulose, % Pentosan....																				
	11.68	10.14	7.97	8.95	7.78	7.60	7.12	6.81	6.33	5.89	24.22	24.74	21.87	20.72	16.20	16.90	17.83	19.01	17.34	19.67
Methyl- pentosan....																				
	1.31	1.24	1.32	1.28	2.73	2.44	2.02	2.09	1.25	1.65	0.58	0.88	1.12	1.13	1.39	1.30	1.47	0.78	1.47	1.60
	66.62	50.69	55.22	69.17	—	54.61	57.29	54.56	57.38	58.18	67.33	68.07	61.17	52.15	59.44	51.55	36.67	34.32	42.45	55.11
	11.05	12.98	24.74	14.04	20.17	26.59	22.42	17.47	24.75	26.91	11.84	15.27	23.23	32.90	23.74	21.92	42.75	48.52	33.22	28.29
β-Cellulose																				
	22.33	36.33	20.04	16.79	—	18.80	19.29	27.97	17.87	14.91	20.83	16.66	15.60	14.45	16.82	26.53	20.58	17.16	24.33	16.50

II = Heartwood S = Sapwood

Grams per 100 g. Dry Material

Kind of Wood	Soluble in			Acetic Acid	Methoxyl	Pentosan	Lignin	Cellulose	Pentosan in the Cellulose
	Cold Water	Hot Water	1% NaOH						
Douglas fir, Heartwood:									
Springwood.....	3.00	4.67	15.10	0.62	3.48	11.97	32.61	55.95	8.31
Summerwood.....	2.15	3.76	14.56	0.71	3.40	9.89	29.20	59.35	6.50
Western white pine, Heartwood:									
Springwood.....	3.76	5.16	22.08	1.42	3.68	10.07	26.30	57.60	7.27
Summerwood.....	4.29	5.42	21.47	1.40	3.85	9.82	25.30	60.00	6.94
Loblolly pine, Sapwood:									
Springwood.....	3.28	3.49	11.11	1.28	4.05	11.59	28.12	58.06	8.78
Summerwood.....	2.18	2.97	11.01	1.41	4.18	11.12	26.78	61.21	8.69
Heartwood:									
Springwood.....	7.50	7.16	18.14	1.00	6.17	12.77	26.78	53.44	11.52
Summerwood.....	7.64	6.14	21.19	1.11	6.88	12.12	24.18	52.87	11.20
Catalpa, Sapwood:									
Springwood.....	9.12	12.44	34.45	3.33	4.41	22.39	23.64	50.37	25.94
Summerwood.....	7.29	10.11	27.97	4.45	4.10	22.35	18.68	56.49	22.09
Heartwood									
Springwood.....	7.51	11.65	34.27	3.39	4.97	21.33	24.29	50.38	24.77
Summerwood.....	2.69	5.26	24.15	4.07	3.37	21.50	19.35	58.45	21.24
Red alder, Heartwood:									
Springwood.....	3.02	4.01	20.49	3.69	5.18	22.37	24.70	58.38	22.80
Summerwood.....	3.03	4.16	21.15	3.60	5.55	23.36	23.03	57.16	22.90
White ash									
1. d. 0.68, Sapwood:									
Springwood.....	8.84	10.99	23.71	3.11	5.49	21.45	24.35	49.73	23.14
Summerwood.....	6.13	8.18	19.32	2.76	5.44	20.51	23.68	54.17	20.15
2. d. 0.71, Sapwood:									
Springwood.....	4.04	4.95	17.71	2.76	6.34	20.34	25.57	53.56	19.50
Summerwood.....	2.90	3.57	14.57	2.49	6.01	19.35	23.52	57.66	16.97
3. d. 0.81, Sapwood:									
Springwood.....	7.35	8.38	22.95	2.74	5.80	20.17	23.94	52.34	18.56
Summerwood.....	6.85	7.34	19.64	2.41	7.34	20.52	20.83	57.47	14.33

It should be pointed out in connection with these analytical results that the cellulose values are mostly much too high, because they include considerable amounts of wood polyoses; this is evidenced by the fact that the hydrolyzates contain monoses other than glucose. The pentosan is especially difficult to dissolve out. This is particularly true in the Cross-Bevan chlorination method, which has often been used to determine the cellulose in wood. The "cellulose" values reported are, nevertheless, useful for purposes of comparison.

E. Hägglund determined the cellulose content of spruce wood by in-

direct means (737) and found a value of 41%. The wood was carefully pulped with bisulfite solution; this procedure has been proved not to dissolve any cellulose. The non-cellulose constituents of the sulfite pulp so obtained were then determined.

On the basis of recent analyses (738) the total composition of Swedish spruce wood can be given as follows (in per cent of the weight of the wood):

Cellulose.....		41.5
Wood polyoses		
1. Difficultly hydrolyzable		
Mannan.....	2.9	8.3
Xylan.....	2.2	
Fructan*.....	1.2	
"Glucan".....	2.0	
2. Easily hydrolyzable		
Mannan.....	7.4	16.0
Araban.....	0.5	
Xylan.....	5.4	
Galactan.....	1.9	
"Glucan".....	0.8	
Lignin.....		28.0
Acetyl.....		1.4
Resin, ash, protein, undetermined		4.8
		<hr/> 100.0

* Concerning the presence of fructose in wood, cf., however, p. 153.

The cellulose value of 41.5% is in good agreement with the results obtained in a completely different manner by H. Staudinger and E. Husemann (739), cf. p. 132.

G. Jayme and F. Finck (740) investigated pre-extracted spruce wood, and found a higher cellulose content. The figures they obtained were as follows:

	%
Lignin.....	28.2
Cellulose.....	45.0
Pentosan.....	6.7
Mannan.....	9.9
Galactan.....	0.3
Polyuronic acid.....	2.5*
Acetic acid.....	2.1
Formic acid.....	0.2
Undetermined.....	5.1
	<hr/> 100.0

* Presumably glucuronic acid.

The furfural or pentosan values are much too high when phloroglucinol is used to precipitate the hydrochloric acid condensate from the Tollens distillation, as was usually the case. It is still uncertain whether methyl-pentosan occurs in wood.

It is questionable whether *pectins* occur in wood. The easily saponifiable methoxyl does not necessarily come from pectin.

It is sometimes reported that *wax* is present, in addition to resin and fat. At the present time this appears quite dubious, however. As far as is known, no proofs of the occurrence of wax have yet been offered.

W. E. Cross and B. Tollens (741) were the first to observe the fact, discussed above, that acetic acid is easily split off when wood is hydrolyzed. They found that 1% sulfuric acid splits off 1.06-1.56% of acetic acid from spruce at 110-140° C., and as much as 2% of acetic acid from beech at 130° C.

A. W. Schorger (742) also noticed that the amount of acetic acid formed when wood was heated with dilute sulfuric acid was variable. He obtained comparative values by the following procedure: 2 g. of sawdust was refluxed for 3 hours with 100 cc. of 2.5% sulfuric acid. The acetic acid and other volatile acids were determined in the usual manner, and reported as acetic acid.

The chemical composition of compression wood is interesting. E. Hägglund and S. Ljungren (743), and recently also L. Stockman and E. Hägglund (738) investigated the compression wood from spruce, analyzing both the compression wood and the normal wood from the same section of the trunk. On the basis of these two investigations the following average composition of compression wood can be given. It should, however, be pointed out, that variations may be possible.

C o n s t i t u e n t	% o f t h e W o o d	
	Compression Wood	Normal Wood
Lignin		
In the sulfite pulp	6.5	2.9
In the sulfite waste liquor		
Precipitable with naphthylamine.....	15.6	22.7
Not precipitable with naphthylamine.....	15.9	2.4
Acetyl.....	0.8	1.4
Wood polyoses		
Difficultly hydrolyzable		
Mannan.....	2.1	2.9
Xylan.....	2.4	2.2
Fructan*	0.9	1.2
"Glucan".....	4.0	2.0
Easily hydrolyzable		
Mannan.....	4.0	7.4
Galactan.....	9.5	1.9
Xylan + araban.....	5.2	5.9
"Glucan".....	1.2	0.8
Cellulose.....	27.3	41.5
Resin, ash, protein, residue.....	4.6	4.8
	100.0	100.0

* Concerning the presence of fructose in wood, cf., however, p. 153.

These figures show that the compression wood of spruce contains appreciably more lignin and wood polyoses than the normal wood. The exceptionally high content of galactose in the compression wood is striking. The lignin of the compression wood is characterized by the fact that it is much less easily precipitated after sulfonation than is the lignin of normal wood; this fact is connected with the particle size of the ligno-sulfonic acid.

For information on the chemical composition of *barks*, the reader is referred to a review published by E. F. Kurth (744). The chemistry and utilization of bark has been treated in a publication by the Northeastern Wood Utilization Council (744 a).

VII. Physical Structure and Chemical Composition of the Fiber Wall

The elements of the wood are formed in the cambium, as has been described in the first chapter. After nuclear division has occurred in a cambium cell, a new cell wall is formed between the two new nuclei. As soon as this cell division has been completed, cellulose is deposited on the new cell wall, which thus becomes a "middle lamella" covered on each side by a "primary wall" [also designated as "cambial wall" (745)]. The middle lamella [intercellular substance, adherent layer (745)] is said to contain pectins, probably as calcium pectinate (745 a).

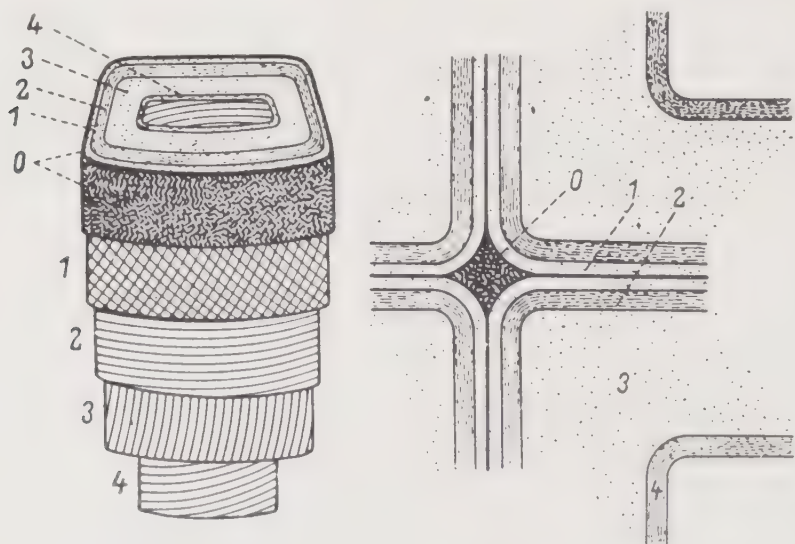


Fig. 53, Fig. 54. Cell walls and intercellular layer. Left, side view, with walls cut away to show the various layers of the cell wall. Right, transverse section. 0, intercellular layer (middle lamella, adherent layer). 1, primary or cambial wall. Secondary wall: 2, outer layer. 3, middle layer. 4, inner spiral layer.

During the next phase, the enlargement of the new cells, the adherent layer and the primary wall (Fig. 53, 54: 0, 1) become thinner, and the secondary wall (Fig. 53, 54: 2) is deposited on the primary wall.

Simultaneous to this thickening of the cell wall, lignification of the adherent layer and the primary as well as the secondary wall takes place. (Concerning the distribution of the lignin throughout the cell wall cf. p. 304.) Lignification, like the preceding phases of division, enlargement, and thickening, is a function of the living cell protoplast.

The primary wall is very thin. It contains cellulose. The pulping process removes most of the adherent layer and primary wall, so that these substances do not occur in technical pulp in very large quantities.

The primary wall and the adherent layer exhibit the same behavior when a section of wood is stained; hence they can not be distinguished from one another by this means. The adherent layer, together with the two neighboring primary walls has previously been incorrectly designated as the middle lamella. The name "compound middle lamella" is a better designation for this region which includes both the actual middle lamella and the two adjacent primary walls.

The main part of the fiber consists of the secondary wall, which can be subdivided into three layers; outer layer, (Fig. 53, 54: 2), middle layer (Fig. 53, 54: 3), and inner spiral layer (Fig. 53, 54: 4).

The outer layer constitutes only a small portion of the fiber; in beech fibers, for example, it amounts to 12%. When swelled, this layer usually appears to consist of spiral bands with a small pitch, but it sometimes appears as a skin with no structure.

Closer examination reveals that the spiral bands consist of several spirals running parallel, and connected by delicate membranes. The membranes consist of fibrils which run nearly perpendicular to the edges of the spirals. Both the fibrils and the edges of the spirals are extensively lignified. The outer layer also contains the pits. Fig. 55 [after H. Dolmetsch, E. Franz, and E.



Fig. 55. Outer layer of the secondary wall of a cell, consisting of a spiral band with three threads.

Correns (746)] shows a spiral band which consists of three threads. Rupture in the direction parallel to the length of the fiber can also occur, especially in the cells of springwood. This layer of the cell is more resistant to certain kinds of attack than is the rest of the secondary layer. It is, for example, difficultly soluble in Schweizer's solution. This insolubility is also characteristic of the nitrate and acetate, and appears in the viscose reaction (747). This is also the reason why balloon and spiral

band swelling are observed on treatment with ammoniacal copper oxide solutions (748). H. F. Lewis and C. A. Richardson (749) found that a sulfite pulp with a high lignin content 17.7%—showed no balloon swelling, but that a pulp with 8.8% of lignin did show it. This may be due to the fact that the highly lignified cambial wall and adherent layer had not been removed from the pulp with high lignin content.

In this connection it should be pointed out, however, that it is not the lignin itself which hinders the balloon swelling of the fibers. Experiments described by E. Hågglund and B. Webjörn (749 a) showed that a spruce holocellulose containing only 1.17% lignin did not swell when treated with phosphoric acid according to the method described by B. Steenberg (750), and furthermore, no swelling could be observed after a two-stage hypochlorite bleach.

The effect of heating of pulp fibers on balloon swelling has been investigated by B. Steenberg (750), who also carried out interesting swelling studies on model fibers, which were prepared by turning a spiral of jute thread around a tube of pure latex rubber and cementing the spiralled thread by means of cellulose lacquer. This model could imitate a large part of the observations made on the swelling of genuine fibers.

The middle layer of the secondary wall is considerably thicker than the outer layer; the larger part of the cellulose of the fiber is therefore found here. On superficial examination of this layer it appears to be completely homogeneous. Actually, however, it consists of a large number of very thin, concentric lamellae. Such lamellae had already been observed in cotton fibers. T. Kerr and I. W. Bailey (751) demonstrated that they are present in the middle layer of fibers of softwood, and H. Dolmetsch, E. Franz, and E. Correns (746) found them in pulp from beech wood, where 12-40 lamella layers were present, depending on the development of the secondary wall. The thickness of the individual lamellae was approximately 1μ when they were very much swelled.

It is assumed that the lamellae are formed by the alternate deposition of denser and less dense cellulose during the day and night. The less dense cellulose may be formed at times when the energy of formation is not sufficient for the crystallization of the cellulose. This amorphous region also serves to bind the crystalline layer which is formed later. The amorphous (less dense) regions react more easily (on hydrolysis, for example); this has actually made possible a separation of the layers.

Mechanical or chemical action causes the lamellae to disintegrate into long, thin threads, *fibrils* or *bundles of fibrils*, which in untreated fibers encircle the fiber axis in the form of spirals of varying pitch. It appears to be possible to split the fibers into fibrils without breaking the main valence

chains of the cellulose. The cellulose chains run parallel with the long axes of the fibrils.

Dolmetsch, Franz, and Correns (746) have found that a transverse splitting of the fiber occurs when fibers damaged by acid are swelled with sodium hydroxide, or when undamaged fibers are treated with phosphoric acid. They explain these phenomena on the assumption that the middle layer of the secondary wall has a spiral structure running transverse to the fiber axis, as is shown in Fig. 56, 57.

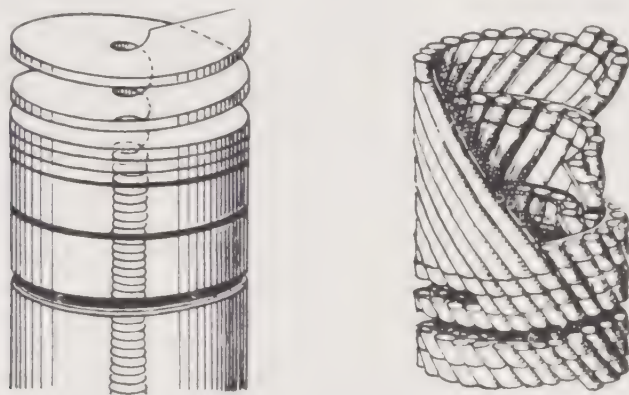


Fig. 56, Fig. 57. Middle layer of the secondary wall of a cell, showing the transverse (to the fiber axis) spiral structure.

These authors believe that the cleavage planes can be separated by the action of suitable swelling-agents without breaking the primary valence chains of the cellulose. The planes are held together by the mutual interactions of the secondary valences of the projecting ends of the cellulose chains; these forces can be overcome only by strong swelling or by mechanical force.

The thickness of the transverse spirals varies from fiber to fiber, and also with the type of wood. The range is $1-2\ \mu$. The pitch is small, being about $2-5^\circ$. The spirals form left-handed screws.

The fibrils can under certain circumstances be split along the cleavage surfaces of the transverse spirals. These fragments are the smallest units into which the cellulose skeleton can be divided without degradation. They contain numerous elliptical or round particles with diameters of the order of $0.6\ \mu$. According to these authors these particles appear to be identical with Farr's particles (752) and with the dermatosomes of Wiesner (753).

The picture which has just been discussed assumes among other things that the degree of polymerization of the cellulose is approximately 3,000, corresponding to a chain length of $1.6\ \mu$. The breadth of the fragments

formed by splitting the fibrils was estimated as 1μ . In this region the cellulose chains were oriented parallel to one another, and closely packed,

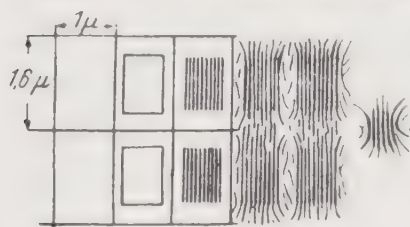


Fig. 58. Orientation and packing of cellulose chains in fibril fragments. The chain length of 1.6μ corresponds to a degree of polymerization of 3,000. The fragment formed by splitting the fibrils is 1μ .

as is shown in Fig. 58. The space between the cellulose bundles may be filled up with wood polyoses and lignin, or with cellulose chains which have a lower degree of polymerization, and which are also, for the most part, more poorly oriented.

H. Dolmetsch (754) has extended and summarized his views of the structure of spruce wood fibers in the schematic diagram, Fig. 59, and in the following table. These views are put forward only with many reservations, for many of the assumed facts are certainly still unproved.

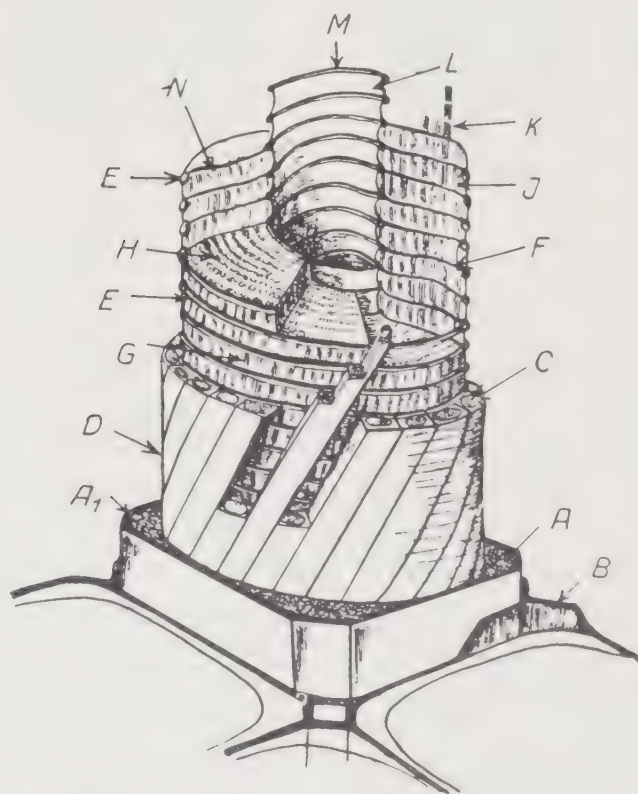


Fig. 59. Schematic diagram of spruce wood fiber, cut away to show the various layers of the cell wall.

A, primary membrane; A₁, thickened edge; B, adherent layer (intercellular layer); C, fibrils of the steeply-spiraled secondary layer; D, cementing substance; E, "outer spirals"; F, cleavage surfaces of the "transverse spirals"; G, surfaces of "transverse spirals"; H, lamellae of the secondary layer; I, K, fibrils of the spiral secondary layer; L, membrane of the lumen; M, inner flat spirals; N, intermediate layers.

		Structures					
		Primary membrane	Isotropic	Outermost envelope of the fiber	1	0.2 μ	
A ₁		Thickened edges	Isotropic	Parallel to longitudinal axis	4-6	(0.5-1) \times 3,000 to 7,000 μ	Originally probably a protein-wax combination; later very much incrustated with a lignin rich in methoxyl
B		Adherent layer (= intercellular substance)	Isotropic	Between the cells		0.1 μ	Pectin, presumably likewise later incrustated
C		Fibrils of the steeply-spiraled secondary layer	Longitudinally fibrillated	Tangential, at an angle of 30-40° to the longitudinal axis	15-25	1.2 \times 4,200 to 9,800 μ	Cellulose, later incrustated with lignin
D		Cementing substance	Isotropic	Interstices between the fibrils			Less-well oriented cellulose and accompanying substances, later also incrustated
E		"Outer spirals" (with small pitch)	Presumably longitudinally oriented	Between the steeply-spiraled layer and the spiral surfaces of the "transverse spirals"	2-6	thickness = 0.6 μ	High-polymetric pentosan, not incrustated
F		Cleavage surfaces of the "transverse spirals"	Isotropic	Between the spiral surfaces of the "transverse spirals"	2-6	0.1 μ	High-polymetric pentosan, not incrustated
G		Surfaces of the "transverse spirals"	Cross fibrillated	Between the lumen and the steeply-pitched fibrillated layer which runs through the fiber transverse to the longitudinal axis	usually 4	Thickness, 1.2-1.7 μ breadth, 4-5 μ	
H		Lamellae of the secondary layer	Longitudinally fibrillated	Concentric cylinders	15-40	< 0.6 μ	Cellulose, hemicellulose, later incrustated with a lignin poor in methoxyl
I		Fibrils of the spiral secondary layer (with small pitch)	Longitudinally fibrillated	Inside the lamellae, at an angle of 10-20° to the longitudinal axis	\approx 100 per lamella	Thickness < 0.5 μ \approx 0.1 μ	Cellulose, later incrustated with a lignin poor in methoxyl
L		Membrane of the lining of the lumen	Unknown		1		Unknown; very resistant
M		Inner flat spirals	Presumably longitudinally fibrillated	In the spaces between the transverse spirals	2-6, usually 4	Thickness = 0.1 μ	Presumably high-polymetric pentosan
N		Intermediate layers	Amorphous	Between the lamellae	approx. 15-40	0.2 μ	Low-polymetric pentosan and substances which accompany cellulose, incrustated with a lignin poor in methoxyl

The view of the chemical and morphological structure of the cell walls described here gives, as yet, no satisfactory answer to the question as to why the beating of pulp fibers yields a material which gives a paper with

high tearing strength; this would hardly be possible if all the fibers were completely disintegrated into fragments corresponding to the fibrils.

A further difficulty, if it proves to be correct, would be the assertion that the molecular size of native cellulose is much larger than that assumed ($= 3,000$ glucose units). According to E. Pacsu (cf. p. 90) native cellulose possesses an indefinitely high molecular weight. Such huge macromolecules could not find space in the fragments.

In the opinion of many investigators, the so-called "skin substance" is an important constituent of the fibers (755). This is evidently identical with the outer layer of the secondary wall. It is also asserted that not only the fibers but also the lamellae and the fibrils are enclosed in a skin substance. This is supposed

Fig. 60. Schematic diagram showing the skin system which takes the form of spiral bands, alternating with the fibrils of the lamellae. The fibrils are the vertical rod-like structures.

to have a decisive influence on the strength of the fibers. It is not known what substance makes up this skin. According to K. Lauer (756) the skin is nothing else but a layer of amorphous constituents lying between the individual spiral bands, and serving to bind together the micellar layers.

This concept has been further developed by Dolmetsch, Franz, and Correns, in connection with their previous ideas on the structures of the fibers. They believe that they have proved that film-like structures actually are present between the fibril layers of the various lamellae. These films have a different chemical composition from the fibrils, and contain "substances which accompany the cellulose." Especially the structure differs from that of the fibrils. The position of this skin-substance is shown schematically in Fig. 60 and 61.

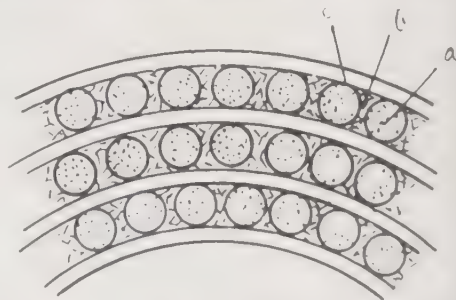
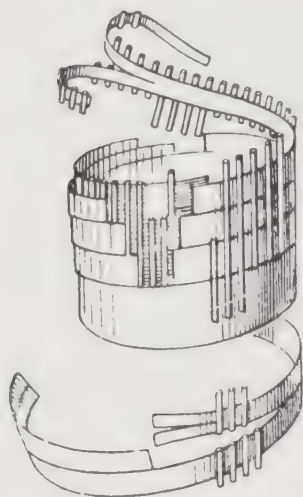


Fig. 61. Imaginary arrangement of the fundamental structures as seen in a transverse section of the secondary layer (schematic representation.)

a, crystalline region of the fibrils. *b*, intermediate region which is less-highly ordered. *c*, layer of connecting skin substance of unknown structure.

It has already been emphasized that the view here given as to the fine structure of the fiber walls is by no means certain in all details. The work of W. Schramek and A. L. Stenzel (747) has in any case confirmed the fact that the outer layer of the secondary wall is more resistant to chemical

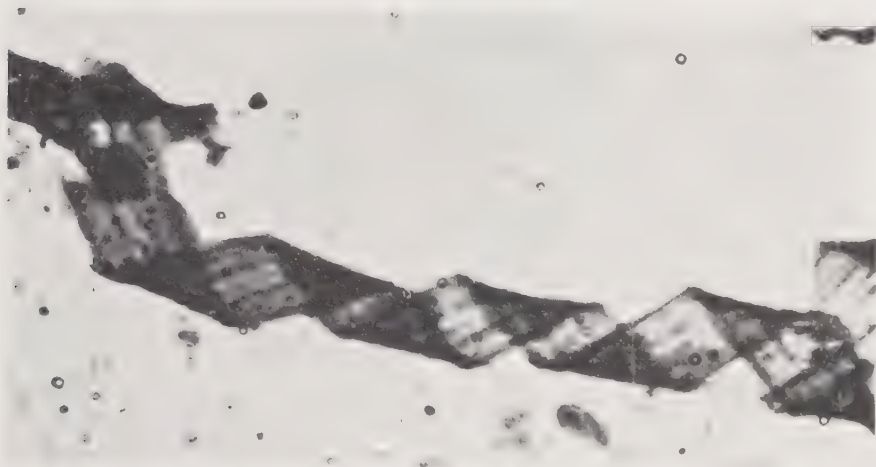


Fig. 62. A band of outer skin substance from a wood tracheid, showing openings at regular intervals along the long axis. Magnified 200 times. (After Schramek.)



Fig. 63. The break-up of the longitudinal fibril structure of a wood tracheid, caused by the chemical reaction which proceeds preferentially in the direction perpendicular to the fiber axis. The fibrils have been separated into fragments which are attached to a transverse reinforcing structure. Magnified 150 times. (After Schramek.)

attack, and can be freed from the other two layers by the viscose reaction (Fig. 62) if sufficient care is taken. They have also shown that further xanthogenation results in the laying bare of new layers which show both longitudinal strengthening and transverse structures which are illustrated in the photographs of Schramek (Fig. 63, 64).

As has been mentioned above, however, it is difficult to understand

why the wet beating of fibers causes them to be split easily in the direction of the fiber, yielding fibrils whose length is several times that of the macromolecules [as E. Husemann (757) has proved] and whose thickness



Fig. 64. Spiral ridge with fringe-like fibril fragments like those shown in the preceding figure. Magnified 75 times. (After Schramek.)

is not dependent on any characteristics of the fiber, but upon the rigor of the treatment. The thickness of the fibrils lies between 60 and 100 μ . This is quite different from the dimensions of the fundamental particles (1 μ), and is also in poor agreement with the diameter of the "fundamental fibrils" of K. Hess (758).

REFERENCES TO CHAPTER III, SECTIONS IV, V, VI, AND VII
(Pages 181-366)

1. Gay-Lussac, J. L., and Thenard, L. J., quoted by Bronguiart, Pelouze, and Dumas, *Compt. rend.* **8**, 51 (1839).
2. Petersen, C., and Schödler, F., *Ann.* **17**, 139 (1836).
3. Payen, A., *Compt. rend.* **7**, 1052 (1838).
4. Schulze, F., *Chem. Zentr.* **1857**, 321.
5. Schmidt, E., and co-workers, *Ber.* **54**, 1860, 3241 (1921); **56**, 23, 1438 (1923); **57**, 1834 (1924); **58**, 1394 (1925).
6. Heuser, E., and Merlau, O., *Cellulosechemie* **4**, 101 (1923); Cleve-v. Euler, A., *ibid.* **4**, 109 (1923); Fuchs, W., and Honsig, E., *Ber.* **59**, 2850 (1926).
7. Hilpert, R. S., and Littmann, E., *Ber.* **67**, 1551 (1934); **68**, 16 (1935); Hilpert, R. S., and Hellwege, H., *Ber.* **68**, 380 (1935); Hilpert, R. S., and Peters, O., *Ber.* **68**, 1575 (1935).
8. Cf. also Paloheimo, L., *Biochem. Z.* **214**, 161 (1929).
9. Schütz, F., and Sarten, P., *Cellulosechemie* **21**, 35 (1943); **22**, 1 (1944).
10. Schütz, F., Sarten, P., and Meyer, H., *Holzforschung* **1**, 2 (1947); Schütz, F., *Holzforschung* **2**, 33 (1948).
11. Hilpert, R. S., *Holzforschung* **2**, 39 (1948).
12. Lange, P. W., *Svensk Papperstidn.* **47**, 262 (1944); **48**, 241 (1945); **50**, No. 11 B (Jubilee Vol. E. Hägglund), 130 (1947).
13. Frey-Wyssling, A., *Holzforschung* **2**, 37 (1948).
14. Hess, K., *Holzforschung* **2**, 44 (1948).
- 14 a. Jayme, G., *Holzforschung* **2**, 65 (1948).
15. Hägglund, E., *Ber.* **56**, 1966 (1923); Hägglund, E., and Björkman, C. B., *Biochem. Z.* **147**, 75 (1924).
16. Runge, F. F., *J. prakt. Chem.* [1] **1**, 24 (1834); *Poggendorff's Annalen* **31**, 65 (1834).
17. Covelli, E. *Chem.-Ztg.* **25**, 684 (1901).
18. Wurster, C., *Ber.* **20**, 808 (1887).
19. Dukelsky, S., *Papier-Fabr.* **10**, 6 (1912).
20. Ihl, A., *Chem.-Ztg.* **14**, 1571 (1890).
21. Czapek, F., *Biochemie der Pflanzen*, vol. I, Jena, 1913, p. 689.
22. Wiesner, J. v., and Lippman, E. O. v., after Grafe, V., *Monatsh.* **25**, 990 (1904).
23. Nickel, E., *Chem.-Ztg.* **11**, 1520 (1887).
24. Czapek, F., *Z. physiol. Chem.* **27**, 141 (1899).
25. Czapek, F., *Biochemie der Pflanzen*, vol. I, Jena, 1913, p. 691.
26. Grafe, V., *Monatsh.* **25**, 987 (1904).
27. Hoffmeister, C., *Ber.* **60**, 2062 (1927).
28. Pauly, H., and Feuerstein, K., *Ber.* **62**, 297 (1929).
29. Wiechert, K., *Papier-Fabr.* **37**, 17 (1939).
30. Adler, E., and Ellmer, L., *Acta Chem. Scand.* **2**, 839 (1948).
31. Zetzsche, F., quoted by Czapek, F., *Biochemie der Pflanzen*, vol. I, Jena, 1913, p. 692.
32. Czapek, F., *Biochemie der Pflanzen*, vol. I, Jena, 1913, p. 692.
33. Cross, C. F., Bevan, E. J., and Briggs, J. F., *Ber.* **40**, 3119 (1907); Cross, C. F., and Bevan, E. J., *Researches on Cellulose*, vol. 3, London, New York, etc., 1912, p. 116; cf. also *J. Chem. Soc.* **95**, 752 (1899).

34. Ungar E., Beiträge zur Kenntnis der verholzten Faser, Dissertation, Zürich, 1914, p. 28; cf. also Kleinert, T., *Cellulosechemie* **18**, 115 (1940).
35. Cf., e.g., König, J., and Hühn, F., Bestimmung der Cellulose in Holzarten und Gespinnstfasern, Berlin, 1912, p. 26.
36. Cf. Etti, C., *Monatsh.* **3**, 637 (1882); Wenzel, F., *Monatsh.* **34**, 1943 (1913); Ungar, E., Dissertation, Zürich, 1914.
37. Fuchs, W., Die Chemie des Lignins, Berlin, 1926, p. 14.
38. Jonas, K. G., *Wochbl. Papierfabr.* **56**, special issue No. 24 A, 85 (1925).
39. Klason, P., *Medd. Sveriges Kem. Industrikontor* **5**, 16 (1922).
40. Hägglund, E., and Johnson, T., *Biochem. Z.* **187**, 98 (1927); cf. also Podbreznik, F., *Chem. Zentr.* **1921**, **I**, 1212.
41. Hess, K., and Heumann, K. E., *Ber.* **75**, 1802 (1942).
42. Zechmeister, L., Dissertation, Zürich, 1913.
43. Cf. also Renker, M., *Papier-Fabr. Fest- u. Auslandsheft*, **1910**, Heuser, E., and Sieber, R., *Z. angew. Chem.* **26**, 801 (1913).
44. Crocker, E. C., *Ind. Eng. Chem.* **13**, 625 (1921).
45. Ihl, A., *Chem.-Ztg.* **13**, 560 (1889); **15**, 201 (1891); cf. Nickel, E., *Chem.-Ztg.* **17**, 1243 (1893).
46. Klason, P., *Ber.* **53**, 711 (1920).
47. Singer, M., *Monatsh.* **3**, 395 (1882); Hoffmeister, W., *Landw. Jahrb.* **17**, 260 (1888); Helger, R., *Flora* **73**, 46 (1890); Lindsey, F. B., and Tollens, B., *Ann.* **267**, 341 (1891); Ellram, W., *Chem. Zentr.* **1896**, **II**, 99; Lippman, E. O. v., *Ber.* **37**, 4521 (1904).
48. Richter, O., *Z. wiss. Mikroskop.* **22**, 383 (1905).
49. Seliwanoff, Th., *Botan. Centr.* **45**, 279 (1891).
50. Freudenberg, K., Tannin, Cellulose, Lignin. Berlin, 1933, p. 130; Freudenberg, K., and Hess, H., *Ann.* **448**, 121 (1926).
51. Kürschner, K., *Tech. u. Chem. Papier- u. Zellstoff-Fabr.* **26**, 61 (1929).
52. Klason, P., *Ber.* **56**, 300 (1923); **62**, 635 (1929).
53. Adler, E., Björkqvist, K. J., and Häggroth, S., *Acta Chem. Scand.* **2**, 93 (1948).
54. Powick, W. C., *J. Agr. Research* **26**, 323 (1923); *Ind. Eng. Chem.* **15**, 66 (1923).
55. Podbreznik, F., *Pulp Paper Mag. Can.* **27**, 229 (1929).
56. Wiechert, K., *Papier-Fabr.* **37**, 17, 30 (1939).
57. Seliwanoff, Th., *Botan. Centr.* **45**, 279 (1891).
58. Unger, E., and Jäger, R., *Ber.* **36**, 1222 (1903).
59. Lechner, R., and Illig, R., *Biochem. Z.* **299**, 174 (1938); Gierisch, W., *Cellulosechemie* **6**, 84 (1925).
60. Pavolini, T., *Riv. ital. essenze, profumi e piante offic.* **15**, 171 (1933); *Chem. Abstr.* **28**, 6126 (1934).
61. Brauns, F. E., *J. Am. Chem. Soc.* **61**, 2120 (1939); *Paper Trade J.* **111**, No. 14, 35 (1940).
- 61 a. Adler, E., and Häggroth, S., *Acta Chem. Scand.* **3**, 86 (1949).
62. Cross, C. F., and Bevan, E. J., *J. Soc. Chem. Ind. London* **12**, 104 (1893); Haller, R., *Farben-Ztg.* **26**, 157 (1915); **30**, 29 (1919); Crocker, E. C., *Ind. Eng. Chem.* **13**, 627 (1921).
63. Payen, A., *Compt. rend.* **29**, 249 (1849).
64. Cross, C. F., and Bevan E. J., *Chem. News* **42**, 80 (1880); Cellulose, N. Y., 1918, p. 134.
65. Heuser, E., and Sieber, R., *Z. angew. Chem.* **26**, 801 (1913).

- 65 a. Abadie, F. A., *Norsk Skogindustri* **3**, 290 (1949).
66. Isenberg, I. H., and Buchanan, M. A., *J. Forestry* **43**, 12 (1945).
- 66 a. Pew, J. C., private communication.
- 66 b. Combes, R., *Bull. sci. pharmacol.* **13**, 293, 270 (1906).
67. Mäule, C., Verhalten verholzter Membranen gegen Kaliumpermanganat, Habilitationsschrift, Stuttgart, 1901; *Beitr. wiss. Bot.* **4**, 166 (1900).
68. Cf. also Schorger, A. W., *Ind. Eng. Chem.* **9**, 566 (1917).
69. Cf. also Lamarlière, L. G. de, *Rev. gén. botan.* **15**, 149 (1903).
70. Crocker, E. C., *Ind. Eng. Chem.* **13**, 635, 801 (1921).
71. Cf. also Sharma, F. D., *J. Forestry* **2**, 476 (1922), quoted by Schorger, A. W., *The Chemistry of Cellulose and Wood*, N. Y., 1926, p. 124.
72. Campbell, W. G., and McGowan, J. C., *Nature* **143**, 1022 (1939).
73. Mitchell, C. A., *Analyst* **48**, 2 (1923).
74. Casparis, P., *Chem. Abstr.* **15**, 1333 (1921).
75. Grüss, J., *Ber. deut. botan. Ges.* **38**, 361 (1920).
76. Schorger, A. W., *The Chemistry of Cellulose and Wood*, N. Y., 1926, p. 122.
77. Jayme, G., and Harders-Steinhäuser, M., *Holzforschung* **1**, 33 (1947).
78. Klason, P., Beiträge zur Kenntnis der chemischen Zusammensetzung des Fichtenholzes, Berlin, 1911, p. 34.
79. Freudenberg, K., Janson, A., Knopf, E., and Haag, A., *Ber.* **69**, 1415 (1936).
80. Aronowsky, S. I., and Gortner, R. A., *Ind. Eng. Chem.* **28**, 1270 (1936).
81. Häggglund, E., and Sandelin, O., *Svensk Kem. Tid.* **46**, 83 (1934).
82. Hibbert, H., Brauns, F., and Buckland, I. K., *Can. J. Research* **13 B**, 61 (1935).
83. Holmberg, B., *Ing. Vetenskaps Akad. Handl. No.* **103**, 64 (1930).
84. Cf. Klason, P., *Tek. Tid. Uppl. C. Kemi* **23**, 55 (1893); Holmberg, B., and Runius, S., *Svensk Kem. Tid.* **37**, 89 (1925); Häggglund, E., and Urban, H., *Cellulosechemie* **8**, 69 (1927); **9**, 49 (1928); Hibbert, H., and Brauns, F., *Can. J. Research* **13 B**, 28 (1935).
85. Cf. Häggglund, E., *Holzchemie*, 2nd ed., Leipzig, 1939, p. 205.
86. Brauns, F. E., *J. Org. Chem.* **10**, 211 (1945).
- 86 a. Buchanan, M. A., Brauns, F. E., and Leaf, R. L., jr., *J. Am. Chem. Soc.* **71**, 1297 (1949).
87. Steeves, W. H., and Hibbert, H., *J. Amer. chem. Soc.* **61**, 2194 (1939).
88. Guillemonat, A., and Traynard, P., *Bull. soc. chim. France* [5] **9**, 484 (1942).
- 88 a. Stumpf, W., and Freudenberg, K., *Angew. Chem.* **62**, 537 (1950).
89. Häggglund, E., and Johnson, T., *Biochem. Z.* **202**, 439 (1928); Häggglund, E., Johnson, T., and Busch, H., *Finnish Paper Timber J.* **16**, 282 (1934).
90. Häggglund, E., and Ringbom, A., *Z. anorg. u. allgem. Chem.* **150**, 231 (1926); **169**, 96 (1928).
91. Erdtman, H., *Svensk Papperstidn.* **48**, 75 (1945).
92. Häggglund, E., Erdtman, H., Aulin-Erdtman, G., and Lindgren, B., *Svensk Papperstidn.* **49**, 199 (1946).
93. Kullgren, C., *Svensk Kem. Tid.* **44**, 15 (1932).
94. Larsson, A., *Svensk Papperstidn.* **46**, 123 (1943).
95. Klason, P., *Tek. Tid. Uppl. C. Kemi* **23**, 53 (1893).
96. Freudenberg, K., Belz, W., and Niemann, Chr., *Ber.* **62**, 1554 (1929).
97. Freudenberg, K., *Cellulosechemie* **12**, 263 (1931).
98. Fuchs, W., Elsner, B., and Stix, B., *Ber.* **52**, 2281 (1919); **53**, 886 (1920); **54**, 245 (1921); **55**, 658 (1922); **57**, 1225 (1924).
99. Bucherer, H., *Z. angew. Chem.* **17**, 1068 (1904); *Ber.* **53**, 1457 (1920).

100. Klason, P., *Svensk Kem. Tid.* **9**, 133 (1897).
101. Hägglund, E., and Carlsson, G. E., *Biochem. Z.* **257**, 467 (1933); Hägglund, E., *Zellstoff u. Papper* **13**, 261 (1933).
102. Freudenberg, K., *Ann.* **518**, 72 (1935); Freudenberg, K., Meister, M., and Flickinger, E., *Ber.* **70**, 500 (1937).
103. Freudenberg, K., Meister, M., and Flickinger, E., *Ber.* **70**, 500 (1937).
104. Erdtman, H., *Ann.* **503**, 283 (1933).
105. Richtzenhain, H., *Ber.* **72**, 2152 (1939).
- 106 a. Hägglund, E., and Holmberg, J., in Hägglund, E., *Holzchemie*, 2nd ed., Leipzig, 1939, p. 147.
- 106 b. Lautsch, W., and Piazzolo, G., *Cellulosechemie* **22**, 48 (1944).
- 106 c. Peniston, Q. P., and McCarthy, J. L., *J. Am. Chem. Soc.* **70**, 1329 (1948).
- 106 d. Aulin-Erdtman, G., *Tappi* **32**, 160 (1949).
107. Kratzl, K., and Däubner, H., *Ber.* **77**, 519 (1944).
108. Russell, A., *J. Am. Chem. Soc.* **70**, 1060 (1948).
109. Ritter, D. M., Pennington, D. E., Olleman, E. D., Wright, K. A., and Evans, T. E., *Science* **107**, 20 (1948).
- 109 a. Kratzl, K., Däubner, H., and Siegens, U., *Monatsh. Chemie* **77**, 146 (1947).
- 109 b. Kratzl, K., *Monatsh. Chemie* **78**, 392 (1948).
- 109 c. Tiemann, F., *Ber.* **31**, 3297 (1898).
- 109 d. Dodge, F. D., *Amer. Parfumer* **31**, No. 3, 67 (1936).
- 109 e. Adler, E., and Häggroth, S., unpublished results.
110. Klason, P., *Ber.* **62**, 2523 (1929); **63**, 792 (1930).
111. Aulin-Erdtman, G., Björkman, A., Erdtman, H., and Hägglund, S. E., *Svensk Papperstidn.* **50**, No. 11B (Jubilee Vol. E. Hägglund), 81 (1947).
112. Holmberg, B., *Papir-Journalen* **23**, 81, 92 (1935).
113. Baeyer, A., and Villiger, V., *Ber.* **35**, 3016 (1902).
114. Berg, G. Ax:son, and Holmberg, B., *Svensk Kem. Tid.* **47**, 257 (1935); Hedén, S., and Holmberg, B., *Svensk Kem. Tid.* **48**, 207 (1936).
115. Hibbert, H., *J. Am. Chem. Soc.* **61**, 725 (1939).
116. Lindgren, B. O., *Acta Chem. Scand.* **1**, 779 (1948); **3**, 1011 (1949).
117. Erdtman, H., and Leopold, B., *Acta Chem. Scand.* **2**, 535 (1948); **3**, 1358 (1949).
- 117 a. Lindgren, B. O., *Acta Chem. Scand.* **4**, 1365 (1950); *ibid.*, in press.
118. Freudenberg, K., Lautsch, W., and Piazzolo, G., *Cellulosechemie* **22**, 97 (1944).
119. Freudenberg, K., and Walch, H., *Ber.* **76**, 305 (1943).
120. Erdtman, H., *Svensk Papperstidn.* **46**, 226 (1943).
121. Erdtman, H., Lindgren, B. O., and Pettersson, T., *Acta Chem. Scand.* **4**, 228 (1950).
- 121 a. Hägglund, E., and Menzinsky, G., *Svensk Papperstidn.* **48**, 19 (1945).
- 121 b. Hägglund, E., *Finnish Paper Timber J.* **16**, 383 (1934).
- 121 c. Erdtman, H., *Svensk Papperstidn.* **42**, 344 (1939).
- 121 d. Erdtman, H., *Svensk Papperstidn.* **43**, 255 (1940).
- 121 e. Erdtman, H., *Cellulosechemie* **18**, 83 (1940).
- 121 f. Erdtman, H., *Tappi* **32**, 71 (1949).
- 121 g. Erdtman, H., *Tappi* **32**, 75 (1949).
- 121 h. Erdtman, H., *Tappi* **32**, 303 (1949).
- 121 i. Erdtman, H., and Pettersson, T., *Acta Chem. Scand.* **4**, 971 (1950).
122. Aulin-Erdtman, G., *Svensk Papperstidn.* **47**, 91 (1944).
- 122 a. Jones, E., Jr., *Tappi* **32**, 311 (1949).
123. Lange, P. W., *Svensk Papperstidn.* **50**, No. 11 B 130 (1947).

- 123 a. Buckland, I. K., Brauns, F. E., and Hibbert H., *Can. J. Res.* **13 B**, 61 (1935).
- 123 b. Brauns, F. E., and Brown, D. S., *Pulp Paper Mag. Can.* **38**, 753 (1937); *Ind. Eng. Chem.* **30**, 779 (1938).
- 123 c. Freudenberg, K., Engler, K., Flickinger, E., Sobek, A., and Klink, F., *Ber.* **71**, 1810 (1938).
124. Hägglund, E., *Holz Roh- u. Werkstoff* **4**, 233 (1941); cf. also Ahlm, C. E., *Paper Trade J.* **113**, No. 13, 115 (1941).
- 124 a. Enkvist, T., Moilanen, M., and Alfredsson, B., *Svensk Papperstidn.* **52**, 517 (1949).
125. Enkvist, T., *Svensk Papperstidn.* **51**, 225 (1948).
126. Enkvist, T., and Hägglund, E., *Svensk Papperstidn.* **53**, 85 (1950).
127. Waentig, P., and Gierisch, W., *Z. angew. Chem.* **32**, 173 (1919); Waentig, P. and Kerenyi, E., *Zellstoffchem. Abhandl.* **1**, 65 (1920); *Papier-Fabr.* **18**, 920 (1920).
128. Pauly, H., *Ber.* **67**, 1177 (1934); cf. also Wedekind, E., and Garre, G., *Z. angew. Chem.* **41**, 107 (1928).
129. Ungar, E., Dissertation, Zürich, 1914, p. 52.
130. Hägglund, E., *Svensk Kem. Tid.* **35**, 2 (1923); *Tek. Tid. Uppl. C. Kemi* **63**, 65 (1933).
131. Freudenberg, K., Tannin, Cellulose, Lignin. Berlin, 1933, p. 123; Rassow, B., and Zickmann, P., *J. prakt. Chem.* [2] **123**, 189 (1929).
132. Freudenberg, K., Lautsch, W., and Engler, K., *Ber.* **73**, 167 (1940).
133. Creighton, R. H. J., Gibbs, R. D., and Hibbert, H., *J. Am. Chem. Soc.* **66**, 32 (1944).
134. Lautsch, W., Plankenhorn, E., and Klink, F., *Angew. Chem.* **53**, 450 (1940).
135. Holmberg, B., *Svensk Kem. Tid.* **53**, 415 (1941).
136. Holmberg, B., *Ber.* **75**, 1760 (1942).
137. Hägglund, E., *Svensk Kem. Tid.* **37**, 116 (1925); **38**, 177 (1926).
138. Hägglund, E., *Finnish Paper Timber J.* **11**, 64 (1929).
139. Hägglund, E., *Finnish Paper Timber J.* **16**, 383 (1934).
140. Hägglund, E., and Johnson, T., *Biochem. Z.* **250**, 221 (1932).
141. Kullgren, C., *Svensk Papperstidn.* **36**, 499 (1933).
142. Kullgren, C., and Du Rietz, C., *Svensk Kem. Tid.* **42**, 179 (1930); **43**, 99, 161 (1931); **44**, 15 (1932); **45**, 185 (1933); **46**, 136 (1934); **49**, 52 (1937).
143. Öman, E., *Svensk Papperstidn.* **28**, 534 (1925).
144. Kullgren, C., *Svensk Kem. Tid.* **44**, 15 (1932).
145. Hägglund, E., and Waller, A., *Finnish Paper Timber J.* **16**, 383 (1934); Hägglund, E., and Sävö, G., *Svensk Papperstidn.* **40**, 23 (1937).
146. Brauns, F. E., and Brown, D. S., *Pulp Paper Mag. Can.* **38**, 753 (1937); *Ind. Eng. Chem.* **30**, 779 (1938).
147. Tollens, B., and Lindsey, J. B., *Ann.* **267**, 341 (1892).
148. Klason, P., *Arkiv Kemi, Mineral. Geol.* **3**, No. 5, 9 (1908).
149. Melander, K., *Medd. Pappersmassекontoret* No. 29 (1921); No. 35 (1921); *Cellulosechemie* **2**, 69 (1921).
150. Hönig, M., and Spitzer, J., *Monatsh.* **39**, 1 (1917).
151. Procter, H. R., and Hirst, S., *J. Soc. Chem. Ind. London* **28**, 293 (1909).
152. Klason, P., *Ber.* **53**, 705, 1862, 1864 (1920).
153. Hintikka, S. V., *Cellulosechemie* **2**, 63 (1921).
154. Melander, K., *Cellulosechemie* **2**, 69 (1921); **4**, 93 (1923); cf. also Dorée, C., and Hall, L., *J. Soc. Chem. Ind. London* **43**, 257 (1924).
155. Hägglund, E., *Cellulosechemie* **6**, 29 (1925); Klason, P., *Svensk Papperstidn.* **30**, 198 (1927).

156. Hägglund, E., *Svensk Kem. Tid.* **42**, 159 (1930).
157. Klason, P., III Nordiska Kemistmötets Förhandlingar, Helsingfors, 1926, p. 215.
158. Freudenberg, K., Sohns, F., and Janson, A., *Ann.* **518**, 62 (1935).
159. Hennig, T., *Papier-Fabr.* **30**, 179 (1932).
160. Noll, A., *Papier-Fabr.* **36**, 41 (1938); *Papier-Fabr. Wochbl. Papierfabr.* **1944**, 39.
161. Erdtman, H., *Svensk Kem. Tid.* **53**, 201 (1941).
162. Hägglund, E., and Johnson, T., *Svensk Papperstidn.* **34**, 553 (1931).
163. Erdtman, H., *Svensk Papperstidn.* **45**, 315, 374, 392 (1942).
164. Erdtman, H., Ericson, P., Hägglund, E., *Svensk Papperstidn.* **46**, 121 (1943).
165. Larsson, A., *Svensk Papperstidn.* **46**, 93 (1943).
166. Heiwinkel, H., *Svensk Papperstidn.* **46**, 123 (1943).
167. Erdtman, H., *Svensk Papperstidn.* **45**, 392 (1942).
168. Adler, E., *Svensk Papperstidn.* **49**, 339 (1946);
169. Borodina, O., *Chem. Zentr.* **1936**, **I**, 4104.
170. Schwabe, K., and Hasner, L., *Cellulosechemie* **20**, 61 (1942); Schwabe, K., and Hahn, E., *Holzforschung* **1**, 42, 79 (1947).
171. Brintzinger, H., *Z. anorg. u. allg. Chem.* **168**, 145 (1927).
172. Jander, G., and Spandau, H., *Z. physik. Chem.* **185 A**, 362 (1939).
173. Spandau, H., and Griess, W., *Ber.* **74**, 366 (1941).
174. Racky, G., *Papier-Fabr.* **39**, 121 (1941).
175. Pennington, D., and Ritter, D. M., *J. Am. Chem. Soc.* **69**, 665 (1947).
- 175 a. Ernsberger, F. M., and France, W. G., *J. Phys. and Colloid Chem.* **52**, 267 (1948).
176. Ögland, N. J., *Svensk Papperstidn.* **47**, 288 (1944).
177. Hiester, N. K., McCarthy, J. L., and Benson, H. K., *Paper Trade J.* **126**, No. 16, 58 (1948).
178. Staudinger, H., and Dreher, E., *Ber.* **69**, 1729 (1936).
179. Cf. also Wedekind, E., Engel, O., Storch, K., and Tauber, L., *Cellulosechemie* **12**, 163 (1931).
- 179 a. Samuelson, O., and Westlin, A., *Svensk Papperstidn.* **50**, No. 11 B (Jubilee vol. E. Hägglund), 149 (1947); *Svensk Papperstidn.* **51**, 179 (1948).
- 179 b. Samuelson, O., *Svensk Kem. Tid.* **60**, 128 (1948).
- 179 c. Regestad, S. O., and Samuelson, O., *Svensk Kem. Tid.* **61**, 9 (1949).
180. Hibbert, H., King, E. G., and Brauns, F., *Can. J. Research* **13 B**, 88 (1935).
181. Hägglund, E., *Finnish Paper Timber J.* **16**, 383 (1934).
182. Tollens, B., and Lindsey, J. B., *Ann.* **267**, 362 (1892).
183. Krause, H., *Chem. Ind.* **29**, 217 (1906).
184. Klason, P., Beiträge zur Kenntnis der chemischen Zusammensetzung des Fichtenholzes, Berlin, 1911, p. 24.
185. Dorée, C., and Hall, L., *J. Soc. Chem. Ind. London* **43**, 257 (1924).
186. Karatejew, A. W., *Chem. Zentr.* **1940**, **II**, 2617.
187. Pedersen, J. H., and Benson, H. K., *Pacific Pulp & Paper Ind.* **14**, No. 8, 48, 80 (1940).
188. Hilpert, R. S., *Hauptversammlungsber. Ver. Zellstoff-u. Papierchemiker u. Ingenieure* **1925**, 41.
- 188 a. Monnberg, R., *Finnish Paper Timber J.* **31**, No. 7 A, 11 (1949).
189. Kratzl, K., and Bleckmann, C., *Experientia* **2**, 24 (1946); *Monatsh.* **76**, 185 (1946).
190. Schwabe, K., and Preu, E., *Cellulosechemie* **21**, 1 (1943).
191. Carpenter, J. S., and Benson, H. K., *Pacific Pulp & Paper Ind.* **14**, No. 12, 17 (1940).

192. Skewes, T. J., and Benson, H. K., *Ind. Eng. Chem.* **31**, 1133 (1939).
193. Longley, K. D., U.S. Pat. 2,419,783 (1947); *Chem. Abstr.* **41**, 5721 (1947).
194. Klason, P., *Arkiv Kemi, Mineral. Geol.* **6**, No. 15, 13 (1917); Hochfelder, L., Beiträge zur Kenntnis der Ligninsubstanzen, Dissertation, München, 1915; Hägglund, E., *Arkiv Kemi, Mineral. Geol.* **7**, No. 8 (1918); Holmberg, B., and Wintzell, T., *Ber.* **54**, 2417 (1921).
195. Melander, K., *Tek. Tid. Uppl. C. Kemi* **48**, 147 (1918); *Medd. Pappersmassekontoret* No. **35**, 7 (1921).
196. Hönig, M., and Fuchs, W., *Monatsh.* **40**, 341 (1919).
197. Heuser, E., and Winsvold, A., *Ber.* **56**, 902 (1923).
198. Frank, A., German Pat. 40,308 (1886).
199. Klason, P., *Tek. Tid. Uppl. C. Kemi* **23**, 49 (1893).
200. Hönig, M., and Fuchs, W., *Monatsh.* **41**, 215 (1920).
201. Tomlinson, G. H., and Hibbert, H., *J. Am. Chem. Soc.* **58**, 348 (1936).
202. Pearl, I. A., and Benson, H. K., *Paper Trade J.* **111**, No. 19, 29 (1940).
203. Pearl, I. A., Bailey, A., and Benson H. K., *Paper Trade J.* **113**, No. 17, 47, (1941).
- 203 a. Peniston, Q. P., and McCarthy, J. L., *J. Am. Chem. Soc.* **70**, 1329 (1948).
204. Grafe, V., *Monatsh.* **25**, 1001 (1904).
205. Kürschner, K., *J. prakt. Chem.* [2] **118**, 238 (1928).
206. Hönig, M., and Ruziczka, W., *Z. angew. Chem.* **44**, 845 (1931).
207. Hanuš, J., *Z. Untersuch. Nahr. u. Genussm.* **10**, 586 (1905); cf. also Pritzker, J., and Jungkunz, R., *Z. Untersuch. Lebensm.* **55**, 428 (1928).
208. Kürschner, K., and Schramek, W., *Tech. u. Chem. Papier- u. Zellstoff-Fabr.* **28**, 65 (1931); **29**, 35 (1932); Kürschner, K., *Tech. u. Chem. Papier- u. Zellstoff-Fabr.* **30**, 1 (1933); cf. also Shorugin, and Smolyaninova, quoted by Tomlinson, G. H., and Hibbert, H., *J. Am. Chem. Soc.* **58**, 345 (1936).
209. Hägglund, E., and Bratt, L. C., *Svensk Papperstidn.* **39**, 347 (1936).
210. Hägglund, E., and Alvfeldt, O., *Svensk Papperstidn.* **40**, 236 (1937).
211. Hägglund, E., and Heiwinkel, H., *Svensk Papperstidn.* **45**, 128 (1942).
212. Hibbert, H., Buckland, I. K., Tomlinson, G. H., and Leger, Fr., *J. Am. Chem. Soc.* **59**, 597 (1937); **60**, 565 (1938).
213. Bell, A., Hawkins, W. L., Wright, G. F., and Hibbert, H., *J. Am. Chem. Soc.* **59**, 598 (1937).
214. Freudenberg, K., Lautsch, W., and Engler, K., *Ber.* **73**, 167 (1940); Freudenberg, K., and Lautsch, W., *Naturwissenschaften* **27**, 227 (1939); Freudenberg, K., *Angew. Chem.* **52**, 362 (1939); cf. also Schulz, L., Schimmel & Co. A.-G., U.S. Pat. 2,187,366 (1940).
215. Lautsch, W., Plankenhorn, E., and Klink, F., *Angew. Chem.* **53**, 450 (1940).
- 216 a. Wacek, A. v., Kratzl, K., and Bézard, A. v., *Ber.* **75**, 1348 (1942).
- 216 b. Kratzl, K., *Ber.* **76**, 895 (1943).
- 216 c. Wacek, A. v., *Ber.* **77**, 85 (1944).
- 216 d. Kratzl, K., *Ber.* **77**, 717 (1944).
- 216 e. Wacek, A. v., and David, E., *Ber.* **70**, 190 (1937).
- 216 f. Kratzl, K., and Khautz, I., *Monatsh.* **78**, 376 (1948).
- 216 g. Kratzl, K., *Monatsh.* **78**, 392 (1948).
- 216 h. Tomlinson, G. H., 2nd, in "Lignin, Chemistry and Utilization," *Northeastern Wood Utilization Council, Bulletin* No. **19**, 32, 53 (1948).
- 216 i. Kratzl, K., *Monatsh.* **78**, 173 (1948); Kratzl, K., and Rettenbacher, F., *ibid.* **80**, 622 (1949).

- 216 k. Kratzl, K., *Oesterreich. Chemiker-Ztg.* **49**, 143 (1948).
- 216 l. Wacek, A. v., and Kratzl, K., *J. Polymer Sci.* **3**, 539 (1948).
- 216 m. Adler, E., and Häggroth, S., *Acta Chem. Scand.* **3**, 86 (1949).
- 216 n. Adler, E., unpublished results.
- 216 o. Wacek, A. v., and Kratzl, K., *Cellulosechemie* **20**, 108 (1942).
217. Wacek, A. v., and Kratzl, K., *Ber.* **78**, 891 (1943).
218. Kratzl, K., *Experientia* **2**, No. 12 (1946).
219. Pearl, I. A., *J. Am. Chem. Soc.* **71**, 2196 (1949).
220. Richtzenhain, H., and Hofe, Chr. v., *Ber.* **72**, 1890 (1939).
221. Cf. Fries, K., and Brandes, E., *Ann.* **542**, 48 (1939); Adler, E., Euler, H. v., and Cedwall, J. O., *Arkiv Kemi, Mineral. Geol.* **15 A**, No. 7 (1941).
222. Richtzenhain, H., *Ber.* **77**, 409 (1944).
223. Pennington, D. E., and Ritter, D. M., *J. Am. Chem. Soc.* **68**, 1391 (1946).
224. Pennington, D. E., and Ritter, D. M., *J. Am. Chem. Soc.* **69**, 187 (1947).
225. Strehlenert, R. W., *Svensk Kem. Tid.* **25**, 28 (1913).
226. Schwalbe, C. G., *Hauptversamlungsber. Ver. Zellstoff- u. Papierchemiker u. Ingenieure* **1923**, 70; Schwalbe, C. G., and Berling, K., *Papier-Fabr.* **27**, 309 (1929).
227. Lautsch, W., *Cellulosechemie* **19**, 69 (1941).
- 227 a. Lautsch, W., and Piazzolo, G., *Ber.* **76**, 486 (1943).
- 227 b. Salvesen, J. P., Hossfeld, R. L., and Lovin, R. L., U. S. Pat. 2,405,450 and 2,405,451 (1946).
228. Klason, P., *Tek. Tid. Uppl. C. Kemi* **23**, 55 (1893); Klason, P., *Beiträge zur Kenntnis der chemischen Zusammensetzung des Fichtenholzes*, Berlin, 1911, p. 12; cf. also Klason, P., and Fagerlind, O., *Arkiv Kemi, Mineral. Geol.* **3**, No. 6 (1908).
229. Grüss, J., *Ber. deut. botan. Ges.* **41**, 48 (1923).
230. Friedrich, A., and Diwald, J., *Monatsh.* **46**, 31 (1925); cf. also Friedrich, A., and Brüda, B., *Monatsh.* **46**, 600 (1925).
231. Holmberg, B., and Runius, S., *Svensk Kem. Tid.* **37**, 189 (1925).
232. Hägglund, E., and Sundroos, B., *Biochem. Z.* **147**, 221 (1924).
233. Friedrich, A., and Diwald, J., *Biochem. Z.* **179**, 376 (1926).
234. Hägglund, E., and Urban, H., *Cellulosechemie* **8**, 69 (1927); **9**, 49 (1928).
235. Cf. also Routala, O., and Sevón, J., *Ann. Acad. Sci. Fennicae* **29 A**, No. 11 (1927).
236. Bailey, A. J., *Paper Trade J.* **111**, No. 6, 27 (1940).
237. Holmberg, B., *Ing. Vetenskaps Akad. Handl.* No. **103**, 8 (1930).
238. Campbell, W. G., *Biochem. J.* **23**, 1225 (1929).
239. Brauns, F. E., and Hibbert, H., *Can. J. Research* **13 B**, 28 (1935).
240. Holmberg, B., and Runius, S., *Svensk Kem. Tid.* **37**, 196 (1925).
241. Hibbert, H., and King, E. G., *Can. J. Research* **14 B**, 12 (1936).
242. Hibbert, H., and Mackinney, H. W., *Can. J. Research* **14 B**, 55 (1936).
243. Hachihama, Y., and Saegusa, H., *J. Soc. Chem. Ind., Japan* **37**, Suppl. binder 771 (1934); *Chem. Abstr.* **29**, 1981 (1935).
244. Bailey, A. J., *Paper Trade J.* **110**, No. 1, 29; No. 2, 29 (1940); **111**, No. 9, 86 (1940).
245. Charbonnier, H. Y., *Paper Trade J.* **114**, No. 11, 31 (1942).
246. Hägglund, E., *Svensk Papperstidn.* **39**, 349 (1936); cf. also Dobland, R. M., Hawkins, W. L., and Hibbert, H., *J. Am. Chem. Soc.* **61**, 2698 (1939).
247. Bailey, A., *J. Am. Chem. Soc.* **64**, 22 (1942).
- 247 a. Bailey, A., *J. Am. Chem. Soc.* **69**, 575 (1947).
- 247 b. Bailey, A., and Brooks, H. M., *J. Am. Chem. Soc.* **68**, 445 (1946).

248. Friedman, L., and McCully, C. R., *Paper Trade J.* **107**, No. 26, 28 (1938).
249. Cramer, A. B., Hunter, M. J., and Hibbert, H., *J. Am. Chem. Soc.* **61**, 509 (1939); cf. also Brawn, J. S., Heddle, R. D., and Gardner, J. A. F., *J. Am. Chem. Soc.* **62**, 3251 (1940); West, E., MacGregor, W. S., Evans, T. H., and Hibbert, H., *J. Am. Chem. Soc.* **65**, 1176 (1943).
250. Hunter, M. J., Cramer, A. B., and Hibbert, H., *J. Am. Chem. Soc.* **61**, 516 (1939); cf. also Temnikova, T. J., *Chem. Zentr.* **1940**, II, 1860.
251. Brickman, L., Pyle, J. J., Hawkins, W. L., and Hibbert, H., *J. Am. Chem. Soc.* **62**, 986 (1940); Brickman, L., Hawkins, W. L., and Hibbert, H., *ibid.* **62**, 2149 (1940).
252. Hewson, W. B., McCarthy, J. L., and Hibbert, H., *J. Am. Chem. Soc.*, **63**, 3041 (1941); cf. also Hewson, W. B., and Hibbert, H., *ibid.* **65**, 1173 (1943).
253. Hewson, W. B., McCarthy, J. L., and Hibbert, H., *J. Am. Chem. Soc.* **63**, 3045 (1941).
254. Hägglund, E., *Papier-Fabr.* **23**, 449 (1925); **27**, 165 (1929).
255. Patterson, R. F., West, K. A., Lovell, E. L., Hawkins, W. L., and Hibbert, H., *J. Am. Chem. Soc.* **63**, 2065 (1941).
256. Cf. also Lovell, E. L., and Hibbert, H., *J. Am. Chem. Soc.* **63**, 2070 (1941).
257. König, J., *Untersuchung landwirtschaftlich und gewerblich wichtiger Stoffe*, 4th ed., Berlin, 1911, p. 292.
258. Hibbert, H., and Phillips, J. B., *Can. J. Research* **3**, 65 (1930).
259. Hibbert, H., and Rowley, H. J., *Can. J. Research* **2**, 357 (1930); Hibbert, H., and Marion, L., *ibid.* **2**, 364 (1930); **5**, 302 (1931); Gray, K. R., King, E. G., Brauns, F., and Hibbert, H., *ibid.* **13**, 35 (1935); Gray, K. R., Brauns, F., and Hibbert, H., *ibid.* **13B**, 48 (1935); cf. also Gibbs, R. D., *ibid.* **12**, 715 (1935).
260. Rassow, B., and Wagner, K., *Wochbl. Papierfabr.* **63**, 103, 161, 243, 303, 342 (1932).
261. Rassow, B., and Neumann, P., *Wochbl. Papierfabr.* **66**, special number, p. 25 (1935).
262. Schütz, F., *Cellulosechemie* **19**, 33 (1941).
263. Freudenberg, K., and Acker, L., *Ber.* **74**, 1400 (1941).
264. Ogait, A., *Cellulosechemie* **22**, 15 (1944).
265. Engel, O., and Wedekind, E., German Pat. 581,806 (1933).
266. Cf. also Wedekind, E., *Cellulosechemie* **17**, 47 (1936).
267. Wedekind, E., *Naturwissenschaften* **23**, 70 (1935); cf. also Küster, W., and Daur, R., *Cellulosechemie* **11**, 4 (1930).
268. Storch, K., *Cellulosechemie* **17**, 49 (1936).
269. Freudenberg, K., Sohns, F., and Janson, A., *Ann.* **518**, 73 (1935).
270. Perrenoud, H., *Kolloid-Z.* **107**, 40 (1944).
271. Harris, E. E., D'Ianni, J., and Adkins, H., *J. Am. Chem. Soc.* **60**, 1467 (1938).
272. Godard, H. P., McCarthy, J. L., and Hibbert, H., *J. Am. Chem. Soc.* **62**, 988 (1940).
- 272 a. Hibbert, H., *Paper Trade J.* **113**, No. 4, 42 (1941); Godard, H. P., McCarthy, J. L., and Hibbert, H., *J. Am. Chem. Soc.* **63**, 3062 (1941).
273. Cooke, L., McCarthy, J. L., and Hibbert, H., *J. Am. Chem. Soc.* **63**, 3052, 3056 (1941).
274. Adkins, H., Frank, R. L., and Bloom, E. S., *J. Am. Chem. Soc.* **63**, 519 (1941).
275. Saeman, J. F., and Harris, E. E., *J. Am. Chem. Soc.* **68**, 2507 (1946).
276. Bühler, F. A., *Papier-Z.* **25**, 3526 (1900); German Pat. 94,467 (1898).
277. Hochfelder, L., Dissertation, München, 1915.

278. Legerer, E., Dissertation, Berlin, 1921; *Cellulosechemie* **4**, 61 (1932); cf. also Harmuth, R., German Pat. 326,705, 328,783 (1919).
279. Jonas, K. G., *Z. angew. Chem.* **34**, 289 (1921); cf. also Schrauth, W., and Quasebarth, K., *Ber.* **57**, 854 (1924).
280. Kalb, L., and Schoeller, V., *Cellulosechemie* **4**, 37 (1923).
281. Herzog, R. O., and Hillmer, A., German Pat. 412,235 (1925).
282. Fuchs, W., *Die Chemie des Lignins*, Berlin, 1926, p. 42.
283. Buckland, F. K., Brauns, F. E., and Hibbert, H., *Can. J. Research* **13 B**, 61 (1935).
284. Hillmer, A., *Cellulosechemie* **6**, 169 (1925); Hägglund, E., and Johnson, T., *Biochem. Z.* **187**, 98 (1927); Wedekind, E., Engel, O., Storch, K., and Tauber, I., *Cellulosechemie* **12**, 163 (1931); Schrauth, W., and Quasebarth, K., *Ber.* **57**, 854 (1924); Niederl, J. B., Smith, R. A., and McGreal, M. E., *J. Am. Chem. Soc.* **53**, 3390 (1931); Freudenberg, K., Tannin, Cellulose, Lignin. Berlin, 1933, p. 126; Freudenberg, K., and Sohns, F., *Ber.* **66**, 265 (1933).
- 284 a. Wacek, A. v., and Däubner-Rettenbacher, H., *Monatsh.* **81**, 266 (1950).
285. Brauns, F. E., and Lane, W. H., *Paper Trade J.* **122**, No. 8, 41 (1946).
286. Pauly, H., Austrian Patent 83,306 (1917); *Ber.* **67**, 1188 (1934).
287. Powell, W. J., and Whittaker, H., *J. Chem. Soc.* **125**, 357 (1924); **127**, 132 (1925).
288. Routala, O., and Sevón, J., *Ann. Acad. Sci. Fennicae* **29 A**, No. 11, 48 (1927).
289. Friedrich, A., *Z. physiol. Chem.* **176**, 127 (1928).
290. Schütz, F., and Knackstedt, W., *Cellulosechemie* **20**, 15 (1942).
291. Freudenberg, K., and Plankenhorn, E., *Ber.* **75**, 857 (1942).
292. Schütz, F., *Cellulosechemie* **18**, 76 (1940).
293. Staudinger, H., *Ber.* **69**, 1729, 1737 (1936).
294. Hägglund, E., and Urban, H., *Cellulosechemie* **9**, 49 (1928).
295. Hägglund, E., *Svensk Papperstidn.* **39**, 347 (1936).
296. MacGregor, W. S., Evans, T. H., and Hibbert, H., *J. Am. Chem. Soc.* **66**, 41 (1944).
297. Hunter, M. J., Wright, G. F., and Hibbert, H., *Ber.* **71**, 734 (1938).
298. Brauns, F. E., and Buchanan, M. A., *J. Am. Chem. Soc.* **67**, 645 (1945).
299. Hägglund, E., and Urban, H., *Cellulosechemie* **8**, 69 (1927).
300. Freudenberg, K., Janson, A., Knopf, E., and Haag, A., *Ber.* **69**, 1415 (1936).
301. Staudinger, H., and Dreher, E., *Ber.* **69**, 1729 (1936).
302. Wright, G. F., and Hibbert, H., *J. Am. Chem. Soc.* **59**, 125 (1937).
303. Holmberg, B., *Ing. Vetenskaps Akad. Handl.* No. **103** (1930); No. **131** (1934).
304. Holmberg, B., *Oesterr. Chem. Ztg.* **43**, 152 (1940).
305. Cf. also Ahlm, C. E., and Brauns, F. E., *J. Am. Chem. Soc.* **61**, 227 (1939).
306. Brauns, F. E., and Buchanan, M. A., *Paper Trade J.* **122**, No. 21, 49 (1946).
307. Holmberg, B., *Ber.* **69**, 115 (1936).
308. Holmberg, B., *Arkiv Kemi, Mineral. Geol.* **21 A**, No. 10 (1946).
309. Wise, L. E., Peterson, F. C., and Harlow, W. M., *Ind. Eng. Chem. Anal. Ed.* **11**, 18 (1939).
310. Fischer, E., and Bower, R. S., *J. Am. Chem. Soc.* **63**, 1881 (1941).
311. Reid, J. D., Dryden, E. C., and Aronowsky, S. I., *Paper Trade J.* **113**, No. 7, 27 (1941).
312. Hess, K., and Heumann, K. E., *Ber.* **75**, 1802 (1942).
313. Hess, K., and Hwang, Y.-C., *Ber.* **77**, 626 (1944).
314. Lange, G., *Z. physiol. Chem.* **14**, 15, 217 (1890).
315. Streeb, E., Dissertation, Göttingen, 1892.
316. Klason, P., *Tek. Tid. Uppl. C. Kemi* **23**, 17 (1893).

317. Klason, P., and Segerfelt, B., *Arkiv Kemi, Mineral. Geol.* **4**, No. 6 (1911).
318. Holmberg, B., and Wintzell, T., *Ber.* **54**, 2417 (1921); Holmberg, B., and Anderzén, O., *Ber.* **56**, 2044 (1923).
319. Marshall, H. B., Brauns, F. E., and Hibbert, H., *Can. J. Research* **13 B**, 103 (1935); cf. also Brauns, F. E., and Grimes, W. S., *Paper Trade J.* **108**, No. 11, 40 (1939).
320. Pringsheim, H., and Fuchs, W., *Ber.* **56**, 2095 (1923).
321. Mehta, M. M., *Biochem. J.* **9**, 958 (1925).
322. Powell, W. J., and Whittaker, H., *J. Chem. Soc.* **125**, 357 (1921); **127**, 132 (1925).
323. Brauns, F. E., and Lewis, H. F., *Paper Trade J.*, **119**, No. 22, 34 (1944).
324. Yorston, F. H., *Pulp Paper Mag. Can.* **29**, 264 (1930).
325. Gralén, N., *J. Colloid Sci.* **1**, 453 (1946).
326. Enkvist, T., *Svensk Papperstidn.* **51**, 225 (1948).
- 326 a. Brauns, F. E., and Yirak, I. J., *Paper Trade J.* **125**, No. 12, 55 (1947).
327. Holmberg, B., *Ber.* **54**, 2419 (1921).
328. Urban, H., *Cellulosechemie* **7**, 73 (1926).
329. Philipps, M., and Goss, M. J., *J. Am. Chem. Soc.* **53**, 768 (1931); **54**, 1518 (1932).
330. Philipps, M., and Goss, M. J., *Chem. Zentr.* **1939**, **1**, 3550.
331. Plunguian, M., *Ind. Eng. Chem.* **32**, 1399 (1940); cf. also Brookbank, E. B., *Paper Trade J.* **122**, No. 13, 44 (1946).
332. Adkins, H., Frank, R. L., and Bloom, E. S., *J. Am. Chem. Soc.* **63**, 549 (1941).
- 332 a. Harris, E. E., Saeman, J. F., and Bergstrom, C. B., *Ind. Eng. Chem.* **41**, 2063 (1949).
333. Lautsch, W., *Cellulosechemie* **19**, 86 (1941).
334. Lewis, H. F., Brauns, F. E., Buchanan, M. A., and Brookbank, E. B., *Ind. Eng. Chem.* **34**, 1113 (1943).
335. Brauns, F. E., *Ind. Eng. Chem.* **37**, 70 (1945).
336. Brookbank, E. B., *Paper Trade J.* **122**, No. 13, 44 (1946).
337. Powter, N. B., *Brit. Plastics* **19**, 140 (1947); *Paper Ind. and Paper World* **28**, 1744 (1947).
338. Keilen, I. I., and Pollak, A., *Ind. Eng. Chem.* **39**, 480 (1947).
339. Raff, R. A. V., and Tomlinson 2nd, G. H., *Can. J. Research* **27**, 399 (1949).
340. Lautsch, W., *Die Chemie* **57**, 149 (1944).
341. Neuberg, C., *Biochem. Z.* **76**, 107 (1916).
342. McKee, R. H., *Ind. Eng. Chem.* **38**, 382 (1946); Pelipetz, M. G., Dissertation, Columbia Univ., 1937; Lau, H., *Paper Ind. and Paper World* **23**, 247 (1941); McKee, R. H., U. S. Pat. 2,308,564 (1943).
343. Brewer, C. P., Cooke, L. M., and Hibbert, H., *J. Am. Chem. Soc.* **70**, 57 (1948).
344. Braconnot, H., *Ann. chim. et phys.* [2] **12**, 172 (1819).
345. Schulze, F., Beitrag zur Kenntnis des Lignins und seines Vorkommens im Pflanzenkörper, Rostock, 1856.
346. Klason, P., *Hauptversammlungsber. Ver. Zellstoff- u. Papierchemiker u. Ingenieure* **1908**, 53.
347. König, J., *Chem.-Ztg.* **36**, 1101 (1912).
348. Ungar, E., *Cellulosechemie* **7**, 73 (1926).
349. Klason, P., *Cellulosechemie* **4**, 81 (1923).
350. König, J., and Rump, E., *Z. Untersuch. Nahr.-u. Genussm.* **28**, 177 (1914).
351. Sherrard, E. C., and Harris, E. E., *Ind. Eng. Chem.* **24**, 103 (1932); Harris, E. E., Sherrard, E. C., and Mitchell, R. L., *J. Am. Chem. Soc.* **56**, 889 (1934); Harris, E. E., *ibid.* **58**, 894 (1936).

352. Norman, A. G., *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.*, Oxford, 1937, p. 170.
353. Freudenberg, K., and Ploetz, Th., *Ber.* **73**, 754 (1940); Ploetz, Th., *Cellulosechemie* **18**, 49 (1940).
354. Harris, E. E., *Ind. Eng. Chem.* **32**, 1049 (1940).
355. Béchamp, A., *Ann. chim. et phys.* [3] **48**, 463 (1856); *Compt. rend.* **42**, 1213 (1856); Willstätter, R., and Zechmeister, L., *Ber.* **46**, 2401 (1913).
356. Häggglund, E., *Arkiv Kemi, Mineral. Geol.* **7**, No. 8 (1918).
357. Häggglund, E., in *Über Naturprodukte, Jubilee-Vol. M. Hönig, Dresden and Leipzig, 1923*, p. 24; *Ber.* **56**, 1866 (1923); *Cellulosechemie* **4**, 85 (1923); *Biochem. Z.* **147**, 74 (1924).
358. Odinzow, P. N., *Chem. Zentr.* **1936**, **II**, 4218.
359. Hilpert, R. S., and Littmann, E., *Ber.* **68**, 16 (1935).
360. Hilpert, R. S., and Hellwage, H., *Ber.* **68**, 380 (1935).
361. Freudenberg, K., Richtzenhain, H., Flickinger, E., and Engler, K., *Ber.* **72**, 1805 (1939).
362. Häggglund, E., and Johnson, T., *Biochem. Z.* **202**, 440 (1928); Häggglund, E., *Acta Acad. Aboensis, Math. et Phys.* **2**, No. 4, 10 (1922).
363. Kürschner, K., *Zur Chemie der Ligninkörper, Sammlung chem. u. chem.-tech. Vorträge*, vol. 28, Stuttgart, 1926, p. 71.
364. Häggglund, E., and Johnson, T., *Biochem. Z.* **202**, 440 (1928).
365. Willstätter, R., and Zechmeister, L., *Ber.* **46**, 2403 (1913); Häggglund, E., in *Über Naturprodukte, Jubilee-Vol. M. Hönig, Dresden und Leipzig, 1923*, p. 24.
366. Schlubach, H. H., Elsner, H., and Prochownick, V., *Angew. Chem.* **45**, 245 (1932).
367. Ungar, E., Dissertation, Zürich, 1914.
368. Heuser, E., and Skiöldebrand, K., *Z. angew. Chem.* **32**, 41 (1919).
369. Erdmann, E., *Z. angew. Chem.* **34**, 309 (1921).
370. Fischer, F., and Schrader, H., *Ges. Abhandl. Kenntnis Kohle* **5**, 106 (1922).
371. Fischer, F., and Tropsch, H., in *Über Naturprodukte, Jubilee-Vol. M. Hönig, Dresden and Leipzig, 1923*, p. 8.
372. Pictet, A., and Gaulis, M., *Helv. Chim. Acta* **6**, 627 (1923).
373. Rassow, B., and Zickmann, P., *J. prakt. Chem.* [2] **123**, 189 (1929).
374. Kürschner, K., *Zur Chemie der Ligninkörper, Sammlung chem. u. chem.-tech. Vorträge*, vol. 28, Stuttgart, 1926, p. 71.
375. Fuchs, W., *Die Chemie des Lignins*, Berlin, 1926, p. 162; cf. also Urban, H., *Cellulosechemie* **7**, 73 (1926).
376. Häggglund, E., and Rosenqvist, T., *Biochem. Z.* **177**, 376 (1926).
377. Freudenberg, K., and Adam, K., *Ber.* **74**, 387 (1941); cf. also Fierz-David, H. D., and Hannig, M., *Helv. Chim. Acta* **8**, 900 (1925).
378. Heuser, E., and Winsvold, A., *Ber.* **56**, 902 (1923); *Cellulosechemie* **4**, 49, 62 (1923).
379. Cf. also Freudenberg, K., Harder, M., and Markert, L., *Ber.* **61**, 1760 (1928); Freudenberg, K., Sohns, F., and Janson, A., *Ann.* **518**, 62 (1935).
380. Fischer, F., and Tropsch, H., *Ges. Abhandl. Kenntnis Kohle* **6**, 271 (1923); Häggglund, E., and Björkman, C. B., *Biochem. Z.* **147**, 74 (1924); Rassow, B., and Zickmann, P., *J. prakt. Chem.* [2] **123**, 189 (1929); Petrov, N., *Chem. Abstr.* **30**, 8605 (1936).
381. Sarkar, P. B., *J. Indian Chem. Soc.* **10**, 263 (1933).
382. Häggglund, E., *Svensk Kem. Tid.* **39**, 90 (1927).
383. Suida, H., and Prey, V., *Ber.* **74**, 1916 (1941).

384. Fischer, F., Schrader, H., and Treibs, W., *Ges. Abhandl. Kenntniss Kohle* **5**, 221 (1922); Friedrich, A., *ibid.* **6**, 1 (1923).
385. Sarkar, P. B., *Science and Culture* **2**, 551 (1937).
386. Heuser, E., Roesch, H., and Gunkel, L., *Cellulosechemie* **2**, 13 (1921).
387. Freudenberg, K., and Dürr, W., *Ber.* **63**, 2713 (1930).
388. Cf. Routala, O., and Sevón, J., *Cellulosechemie* **7**, 113 (1926).
389. Kalb, L., Plessmann, F., and Lorenz, H., *Papier-Fabr.* **36**, 453 (1938).
390. Hachihama, Y., and Takemura, W., *J. Soc. Chem. Ind., Japan* **39**, Suppl. binding 239, 362 (1936); **40**, Suppl. binding 354 (1937).
391. Cf. König, F., *Cellulosechemie* **2**, 105 (1921).
392. Friese, H., and Lüdecke, W., *Ber.* **74**, 308 (1941).
393. Schaarschmidt, A., Nowak, P., and Zetzsche, W., *Z. angew. Chem.* **42**, 618 (1929).
394. Wieland, H., *Ber.* **54**, 1776 (1921).
395. Fuchs, W., and Horn, O., *Ber.* **62**, 265 (1929).
396. Freudenberg, K., *Ann.* **518**, 62 (1935).
397. Hägglund, E., and Björkman, C. B., *Biochem. Z.* **147**, 74 (1924).
398. Freudenberg, K., Belz, W., and Niemann, Chr., *Ber.* **62**, 1554 (1929).
399. White, E. V., Swartz, J. N., Peniston, Q. P., Schwartz, H., McCarthy, J. L., and Hibbert, H., *Tech. Assoc. Papers* **24**, 179 (1941).
400. Walde, A. W., *Iowa State Coll. J. Sci.* **9**, 205 (1934).
401. Willstätter, R., and Kalb, L., *Ber.* **55**, 2637 (1922).
402. Schrauth, W., *Z. angew. Chem.* **36**, 149 (1923).
403. Freudenberg, K., Tannin, Cellulose, Lignin. Berlin, 1933, p. 129.
404. Karrer, P., and Bodding-Wiger, B., *Helv. Chim. Acta* **6**, 817 (1927).
405. Fierz-David, H. E., and Hannig, M., *Helv. Chim. Acta* **8**, 900 (1925).
406. Cf. Harris, E. E., D'Ianni, J., and Adkins, H., *J. Am. Chem. Soc.* **60**, 1467 (1938); Harris, E. E., and Adkins, H., *Paper Trade J.* **107**, No. 20, 38 (1938); Freudenberg, K., Lautsch, W., Piazzolo, G., and Scheffer, A., *Ber.* **74**, 171 (1941); Lautsch, W., *Cellulosechemie* **19**, 69 (1941); Lautsch, W., and Piazzolo, G., *Ber.* **76**, 486 (1943).
407. Hachihama, Y., Zyôdai, S., and Umezu, M., *J. Soc. Chem. Ind., Japan* **43**, Suppl. binding 127 (1940).
408. Harris, E. E., Saeman, J., and Sherrard, E. C., *Ind. Eng. Chem.* **32**, 440 (1940).
409. Lautsch, W., *Cellulosechemie* **19**, 69 (1941).
410. Lautsch, W., and Piazzolo, G., *Ber.* **76**, 486 (1943).
411. Freudenberg, K., Zocher, H., and Dürr, W., *Ber.* **62**, 1814 (1929); cf. also Freudenberg, K., and Hess, H., *Ann.* **448**, 131 (1926).
412. Freudenberg, K., Sohns, F., and Janson, A., *Ann.* **518**, 63 (1935).
413. Freudenberg, K., Sohns, F., Dürr, W., and Niemann, Chr., *Cellulosechemie* **12**, 263 (1931).
414. Hägglund, E., and Carlsson, G. E., *Biochem. Z.* **257**, 474 (1933).
415. Freudenberg, K., and Sohns, F., *Ber.* **66**, 262 (1933).
416. Freudenberg, K., Janson, A., Knopf, E., and Haag, A., *Ber.* **69**, 1415 (1936).
417. Wacek, A. v., *Ber.* **63**, 282, 2984 (1930); cf. also *Ber.* **70**, 183 (1937).
418. Freudenberg, K., Lautsch, W., and Piazzolo, G., *Ber.* **74**, 1891 (1941).
- 418 a. Shorygina, N. N., and Kefeli, T. Ya., *Zhur. Obshchei Khim.* **18**, 528 (1948); cf. *Chem. Abstr.* **43**, 3609 (1949).
419. Jackson, E. L., and Hudson, C. S., *J. Am. Chem. Soc.* **52**, 2049 (1937).
- 419 a. Ritchie, P. F., and Purves, C. B., *Pulp Paper Mag. Can.* **48**, No. 12, 74 (1947).
- 419 b. Wald, W. J., Ritchie, P. F., and Purves, C. B., *J. Am. Chem. Soc.* **69**, 1371 (1947).

420. Sarkar, P. B., *Science and Culture* **2**, 489 (1937).
421. Freudenberg, K., Engler, K., Flickinger, E., Sobek, A., and Klink, F., *Ber.* **71**, 1817 (1938).
422. Freudenberg, K., and Lautsch, W., *Naturwissenschaften* **27**, 227 (1939); Freudenberg, K., Lautsch, W., and Engler, K., *Ber.* **73**, 167 (1940);
- 422 a. Creighton, R. H. J., McCarthy, J. L., and Hibbert, H., *J. Am. Chem. Soc.* **63**, 312 (1941).
423. Pearl, I. A., *J. Am. Chem. Soc.* **64**, 1429 (1942); *ibid.*, **72**, 1427 (1950).
424. Erdtman, H., *Proc. Roy. Soc. (London)* **143 A**, 189 (1933).
425. Aulin-Erdtman, G., *Svensk Kem. Tid.* **55**, 116 (1943).
- 425 a. Lautsch, W., and Piazzolo, G., *Ber.* **73**, 317 (1940).
426. Cf. Freudenberg, K., and Sohns, F., *Cellulosechemie* **12**, 271 (1931); Freudenberg, K., and Müller, W. Fr., *Ber.* **71**, 2500 (1938).
427. Cf. Harris, E. E., D'Ianni, J., and Adkins, H., *J. Am. Chem. Soc.* **60**, 1467 (1938).
428. Pepper, J. M., and Hibbert, H., *J. Am. Chem. Soc.* **70**, 67 (1948).
429. Freudenberg, K., and Adam, K., *Ber.* **74**, 387 (1941).
430. Brauns, F., and Hibbert, H., *J. Am. Chem. Soc.* **55**, 4720 (1933).
431. Freudenberg, K., Belz, W., and Niemann, Chr., *Ber.* **62**, 1561 (1929).
432. Freudenberg, K., Tannin, Cellulose, Lignin. Berlin, 1933, p. 119.
433. Freudenberg, K., and Plankenhorn, E., *Ber.* **75**, 864 (1942).
434. Müller, O. A., *Papier-Fabr.* **37**, 213 (1939).
435. Brauns, F. E., *J. Am. Chem. Soc.* **61**, 2126 (1939).
436. Rassow, B., and Gabriel, H., *Cellulosechemie* **12**, 249 (1931).
437. Hägglund, E., and Urban, H., *Cellulosechemie* **8**, 70 (1927).
438. Freudenberg, K., Lautsch, W., and Piazzolo, G., *Ber.* **74**, 1879 (1941).
439. Racky, G., *Cellulosechemie* **20**, 22 (1942).
440. Erdtman, H., *Svensk Papperstidn.* **45**, 374 (1942).
441. Marshall, H. B., Brauns, F., and Hibbert, H., *Can. J. Research* **13 B**, 109 (1935).
442. Hägglund, E., *Biochem. Z.* **206**, 245 (1929).
443. Hägglund, E., and Sandelin, O., *Svensk Kem. Tid.* **46**, 83 (1934).
444. Freudenberg, K., Sohns, F., and Janson, A., *Ann.* **518**, 62 (1935).
445. Urban H., *Cellulosechemie* **7**, 73 (1926).
446. Freudenberg, K., and Hess, H., *Ann.* **448**, 121 (1926); Freudenberg, K., Sohns, F., Dürr, W., and Niemann, Chr., *Cellulosechemie* **12**, 263 (1931).
447. Freudenberg, K., and Walch, H., *Ber.* **76**, 305 (1943); cf. also Freudenberg, K., and Plankenhorn, E., *Ber.* **75**, 857 (1942).
- 447 a. Lemon, H. W., *J. Am. Chem. Soc.* **69**, 2998 (1947).
448. Freudenberg, K., *Das Papier* **1**, 209 (1947); Freudenberg, K., and Dietrich, G., *Ann.* **563**, 146 (1948).
- 448 a. Freudenberg, K., *Das Papier* **3**, 260 (1949).
449. Hägglund, E., *Svensk Kem. Tid.* **35**, 2 (1923); *Tek. Tid. Uppl. C. Kemi* **63**, 65 (1933).
450. Adler, E., *Svensk Papperstidn.* **50**, No. 11B (Jubilee Vol. E. Hägglund), 7 (1947).
451. Wright, G. F., and Hibbert, H., *J. Am. Chem. Soc.* **59**, 125 (1937).
452. Harris, E. E., Sherrard, E. C., and Mitchell, R. L., *J. Am. Chem. Soc.* **56**, 889 (1934).
453. Rassow, B., and Zickmann, P., *J. prakt. Chem. [2]* **123**, 189 (1929); Sarkar, J. B., *J. Ind. Chem. Soc.* **11**, 777 (1934).
454. Hägglund, E., and Holmberg, J., in Hägglund, E., *Holzchemie*, 2nd ed., Leipzig, 1939, p. 201.

455. Dimroth, O., *Ber.* **53**, 484 (1920); **54**, 3058 (1921); **55**, 1231 (1922); **56**, 1375 (1923).
Criegee, R., *Ann.* **481**, 263 (1930).
456. Gray, K. R., Brauns, F., and Hibbert, H., *Can. J. Research* **13 B**, 48 (1935).
457. Pauly, H., *Ber.* **67**, 1177 (1934); cf. also Wedekind, E., and Garre, G., *Z. angew. Chem.* **41**, 107 (1928).
458. Harris, E. E., and Lofdahl, L. J., *J. Am. Chem. Soc.* **63**, 112 (1941).
459. Pauly, H., *Ber.* **81**, 392 (1948).
460. Sandermann, W., *Svensk Papperstidn.* **52**, 365 (1949).
461. Routala, O., and Sevón, J., *Ann. Acad. Sci. Fennicae A* **19**, No. 11, 48 (1927).
462. Hibbert, H., and Moore, R. G. D., *Can. J. Research* **14 B**, 404 (1936).
463. Häggglund, E., and Rosenqvist, T., *Biochem. Z.* **179**, 376 (1926).
464. Freudenberg, K., and Harder, M., *Ber.* **60**, 581 (1927).
465. Freudenberg, K., Tannin, Cellulose, Lignin. Berlin, 1933, p. 122.
466. Häggglund, E., and Bratt, L. C., *Svensk Papperstidn.* **39**, 347 (1936).
467. Sarkar, P. B., *J. Indian Chem. Soc.* **11**, 691 (1934).
468. Freudenberg, K., Engler, K., Flickinger, E., Sobek, A., and Klinck, F., *Ber.* **71**, 1810 (1938).
469. Häggglund, E., and Urban, H., *Biochem. Z.* **207**, 1 (1929).
470. Hunter, M. J., Wright, G. F., and Hibbert, H., *Ber.* **71**, 734 (1938).
471. Freudenberg, K., Klinck, F., Flickinger, E., and Sobek, A., *Ber.* **72**, 217 (1939).
472. Freudenberg, K., *Chem. Ber.* **80**, 149 (1947).
473. Hunter, M. J., and Hibbert, H., *J. Am. Chem. Soc.* **61**, 2196 (1939).
474. Bond, W. J., Goddard, I. G., and Wright, G. F., *Can. J. Research* **25 B**, 535 (1947).
475. Herzog, R. O., and Hillmer, A., *Ber.* **60**, 365 (1927); *Z. physiol. Chem.* **168**, 117 (1927); Hillmer, A., and Hellriegel, E., *Ber.* **62**, 725 (1929); Herzog, R. O., and Hillmer, A., *Ber.* **62**, 1600 (1929); **64**, 1288 (1931); *Papier-Fabr.* **29**, special issue No. 23, 40 (1931); **30**, 205 (1932); Hillmer, A., and Paersch, E., *Z. physik. Chem. A* **161**, 58 (1932); Hillmer, A., *Ber.* **66**, 1600 (1933); Hillmer, A., and Schorning, P., *Z. physik. Chem. A* **167**, 407 (1934); **A 168**, 81 (1934).
476. Hillmer, A., *Ber.* **66**, 1600 (1933).
477. Häggglund, E., and Klingstedt, F. W., *Svensk Kem. Tid.* **41**, 185 (1929); *Z. physik. Chem. A* **152**, 295 (1931).
478. Patterson, R. F., and Hibbert, H., *J. Am. Chem. Soc.* **65**, 1862, 1869 (1943).
479. Aulin-Erdtman, G., *Svensk Papperstidn.* **47**, 91 (1944).
480. Stamm, A. J., Semb, J., and Harris, E. E., *J. Phys. Chem.* **36**, 1574 (1932).
481. Glading, R. E., *Paper Trade J.* **111**, No. 23, 32 (1940).
482. Lange, P. W., *Svensk Papperstidn.* **47**, 262 (1944); **48**, 241 (1945).
- 482 a. Jones, E. J., *J. Am. Chem. Soc.* **70**, 1984 (1948); *Tappi* **32**, 167 (1949).
483. Freudenberg, K., Zocher, H., and Dürr, W., *Ber.* **62**, 1814 (1929); Freudenberg, K., Sohns, F., Dürr, W., and Niemann, Chr., *Cellulosechemie* **12**, 263 (1931).
484. Schütz, Fr., and Sarten, P., *Cellulosechemie* **22**, 1, 114 (1944).
485. Häggglund, E., and Urban, H., *Cellulosechemie* **8**, 69 (1927); **9**, 50 (1928).
486. Wedekind, E., and Katz, J. R., *Ber.* **62**, 1172 (1929).
487. Pauly, H., *Ber.* **67**, 1193 (1934).
488. Staudinger, H., and Dreher, E., *Ber.* **69**, 1734 (1936).
489. Loughborough, D. L., and Stamm, A. J., *J. Phys. Chem.* **40**, 1113 (1936).
490. Braun, E., *Cellulosechemie* **12**, 263 (1931).
- 490 a. Erbring, H., and Peter, H., *Kolloid-Z.* **96**, 47 (1941).
491. Holmberg, B., and Gralén, N., *Ing. Vetenskaps Akad. Handl.* No. **162** (1942).

192. Svedberg, T., and Pedersen, K. O., *Die Ultracentrifuge*, Dresden and Leipzig, 1940.
- 492 a. Hällström, M. af, *Ann. Acad. Sci. Fennicae* **A 34**, No. 5 (1931).
- 492 b. Enkvist, T., *Svensk Papperstidn.* **51**, 225 (1948).
493. Conner, W. P., *J. Chem. Phys.* **9**, 591 (1941).
- 493 a. Freudenberg, K., and Kraft, R., *Chem. Ber.* **83**, 530 (1950).
- 493 b. Freudenberg, K., Siebert, W., Heimberger, W., and Kraft, R., *Chem. Ber.* **83**, 533 (1950).
494. Erdmann, J., *Ann. Suppl.* **5**, 223 (1867).
495. Hoppe-Seyler, F., *Z. physiol. Chem.* **13**, 84 (1889); cf. also Lange, G., *ibid.* **14**, 19 (1890).
496. Cross, C. F., *J. Chem. Soc.* **55**, 199 (1889).
497. Schellenberg, H., *Jahrb. wiss. Botan.* **29**, 248 (1896).
498. Czapek, F., *Z. physiol. Chemie* **27**, 165 (1889).
499. Klason, P., *Ber.* **56**, 300 (1923).
500. Payen, A., *Compt. rend.* **7**, 1052 (1838); **8**, 52 (1839).
501. Fromberg, P. F. H., *J. prakt. Chem.* [1] **32**, 198 (1844).
502. Baumhauer, E. H. v., *J. prakt. Chem.* [1] **32**, 210 (1844).
503. Schulze, F., *Chem. Zentr.* **1857**, 321.
504. Sachsse, R., *Die Chemie und Physiologie der Farbstoffe, Kohlenhydrate und Proteinsubstanzen*, Leipzig, 1877, p. 146.
505. König, J., *Ber.* **39**, 3564 (1906); König, J., and Rump, E., *Z. Untersuch. Nahr. u. Genussm.* **28**, 184 (1914).
506. Wislicenus, H., *Kolloid-Z.* **6**, 17, 87 (1910); **27**, 209 (1921); *Cellulosechemie* **6**, 45 (1925).
507. Cross, C. F., and Bevan, E. L., *Researches on Cellulose*, vol. 3, London, New York, etc., 1912, p. 109; *ibid.* vol. 4, 1922, pp. 152, 170.
508. König, J., and Rump, E., *Z. Untersuch. Nahr.- u. Genussm.* **28**, 177 (1914).
509. Freudenberg, K., Zocher, H., and Dürr, W., *Ber.* **62**, 1814 (1929); Freudenberg, K., Sohns, F., Dürr, W., and Niemann, Chr., *Cellulosechemie* **12**, 263 (1931); Freudenberg, K., *Papier-Fabr.* **30**, 189 (1932); Freudenberg, K., *Tannin, Cellulose, Lignin*. Berlin, 1933, p. 139.
510. Freudenberg, K., *Tannin, Cellulose, Lignin*. Berlin, 1933, p. 145.
511. Urban, H., *Cellulosechemie* **7**, 73 (1926); cf. also Suida, H., and Titsch, H., *Monatsh.* **53/54**, 687 (1929).
512. Karrer, P., and Widmer, F., *Helv. chim. Acta* **4**, 700 (1921).
513. Schorger, A. W., *Chemistry of Cellulose and Wood*, N. Y., 1926, p. 30.
514. Zechmeister, L., *Ber.* **56**, 573 (1923).
515. Peniston, Q. P., McCarthy, J. L., and Hibbert, H., *J. Am. Chem. Soc.* **62**, 2284 (1940); cf. also Friese, H., *Ber.* **62**, 2538 (1929).
516. Friese, H., and Fürst, H., *Ber.* **70**, 1463 (1937); Friese, H., and Lüdecke, W., *Ber.* **74**, 308 (1941).
517. Ludtke, M., *Ber.* **61**, 465 (1928); *Biochem. Z.* **233**, 1 (1931); *Cellulosechemie* **13**, 169 (1932).
518. Bergstrom, H., and Cederquist, K., *Iva* **1933**, 79; *Chem. Zentr.* **1933**, **11**, 2212.
519. Staudinger, H., Dreher, E., and Ekenstam, A. af, *Ber.* **69**, 1099 (1936).
520. Levy, J., and Jahn, E. C., *Paper Trade J.* **109**, No. 23, 45 (1939).
521. Hess, K., Jung, K. Ph., and Heumann, K. E., *Naturwissenschaften* **27**, 770 (1939).
522. Gralén, N., *Dissertation*, Uppsala, 1944,

523. Norman, A. G., and Shrikhande, S. G., *Biochem. J.* **29**, 2259 (1935); Norman, A. G., *The Biochemistry of Cellulose, the Polyuronides, Lignin, etc.*, London and Oxford, 1937, p. 61.
524. Lieser, Th., and Schwind, V., *Ann.* **532**, 104 (1937).
525. Häggglund, E., and Björkman, C. B., *Biochem. Z.* **147**, 76 (1924).
526. Friese, H., Högn, V., and Wille, H., *Ber.* **70**, 1072 (1937); Friese, H., and Stoeck, G., *Ber.* **73**, 1135 (1940).
527. Freudenberg, K., and Keller, R., *Ber.* **72**, 331 (1939).
528. Peterson, W. H., and Snieszko, S., *Zentr. Bakt. Parasitenk. Abt. II.* **88**, 410 (1933).
529. Olson, F. R., Peterson, W. H., and Sherrard, E. C., *Ind. Eng. Chem.* **29**, 1026 (1937).
530. Ploetz, Th., *Ber.* **72**, 1885 (1939); **73**, 57, 61, 74, 79 (1940).
531. Virtanen, A. I., Koistinen, O., and Kiuru, V., *Suomen Kemistilehti* **11 B**, 30 (1938); *Cellulosechemie* **18**, 22 (1940); cf. also Virtanen, A. I., and Koistinen, O. A., *Svensk Kem. Tid.* **56**, 391 (1944); Virtanen, A. I., and Nikkilä, O. E., *Suomen Kemistilehti* **19 B**, 3 (1946).
- 531 a. Virtanen, A. I., *Nature* **158**, 795 (1946).
532. Fernández, O., and Rogueiro, B., *Farm. nueva* **11**, 57 (1946); *Chem. Abstr.* **41**, 3292 (1947).
533. Ritter, G. J., *Ind. Eng. Chem.* **17**, 1194 (1925).
534. Freudenberg, K., *Ber.* **62**, 1814 (1929).
535. Staudinger, M., *Holz Roh- u. Werkstoff* **5**, 193 (1942).
536. Harlow, W. M., *Paper Trade J.* **109**, No. 18, 38 (1939); cf. Harlow, W. M., *Ind. Eng. Chem.* **23**, 419 (1931).
537. Lüdtke, M., *Biochem. Z.* **233**, 1 (1931).
538. Thiessen, R., *Ind. Eng. Chem.* **24**, 1032 (1932).
539. Bailey, A. J., *Ind. Eng. Chem. Anal. Ed.* **8**, 52, 389 (1936).
540. Cf. Forsaith, C. C., *N. Y. State Coll. Forestry Syracuse Univ. Tech. Pub.* **18**, 64 (1926).
541. Harlow, W. M., and Wise, L. E., *Ind. Eng. Chem.* **20**, 720 (1928).
542. Hibbert, H., and Mackinney, H. W., *Can. J. Research* **14 B**, 55 (1936).
543. West, K. A., Hawkins, W. L., and Hibbert, H., *J. Am. Chem. Soc.* **63**, 3038 (1941).
544. Erdtman, H., *Svensk Papperstidn.* **44**, 243 (1941).
545. Hibbert, H., *Ann. Rev. Biochem.* **11**, 183 (1942).
546. Freudenberg, K., *Ann. Rev. Biochem.* **8**, 88 (1939).
547. Freudenberg, K., and Klink, F., *Ber.* **73**, 1369 (1940).
548. Freudenberg, K., *Svensk Kem. Tid.* **55**, 201 (1943).
- 548 a. Richtzenhain, H., *Acta Chem. Scand.* **4**, 589 (1950); *Chem. Ber.* **83**, 488 (1950).
- 548 b. Richtzenhain, H., *Acta Chem. Scand.* **4**, 206 (1950).
- 548 c. Richtzenhain, H., *Svensk Papperstidn.* **53**, 644 (1950).
549. Kawai, S., and Sugiyama, N., *Ber.* **72**, 369 (1939).
550. Erdtman, H., *Ann.* **503**, 286 (1933).
551. Aluin-Erdtman, G., *Svensk Kem. Tid.* **54**, 168 (1942).
552. Freudenberg, K., and Richtzenhain, H., *Ann.* **552**, 126 (1942).
553. Erdtman, H., and Leopold, B., *Acta Chem. Scand.* **3**, 1358 (1949).
554. Fisher, H. E., and Hibbert, H., *J. Am. Chem. Soc.* **69**, 1208 (1947).
555. Eastham, A. M., Fisher, H. E., Kulka, M., and Hibbert, H., *J. Am. Chem. Soc.* **66**, 26 (1944).
556. Fisher, H. E., Kulka, M., and Hibbert, H., *J. Am. Chem. Soc.* **66**, 598 (1944); cf. also Mitchell, L., and Hibbert, H., *ibid.* 602; Gardner, J. A. F., and Hibbert, H., *ibid.* 607.

557. Russell, A., *Science* **106**, 372 (1947); *J. Am. Chem. Soc.* **70**, 1060 (1948).
558. Hewson, W. B., McCarthy, J. L., and Hibbert, H., *J. Am. Chem. Soc.* **63**, 3041 (1941).
559. Freudenberg, K., and Plankenhorn, E., *Ber.* **75**, 861 (1942).
- 559 a. Tiemann, F., and Haarmann, W., *Ber.* **7**, 606 (1874); **8**, 509 (1875).
560. Klason, P., *Arkiv Kemi, Mineral. Geol.* **6**, No. 15, 21 (1917).
561. Rassow, B., and Zschenderlein, A., *Z. angew. Chem.* **34**, 204 (1921).
562. Schwalbe, C. G., and Becker, E., *Z. angew. Chem.* **33**, 14 (1920).
563. Schrauth, W., *Z. angew. Chem.* **36**, 150 (1923).
564. Cleve-v. Euler, A., *Cellulosechemie* **2**, 128 (1921); **3**, 1 (1923); cf. also Jonas, K. G., *Wochbl. Papierfabr.* **56**, special number 24 A, 88 (1925); Odén, S., *Svensk Kem. Tid.* **38**, 122 (1926).
565. Casparis, P., *Pharm. Monatsh.* **1**, 121 (1920).
566. Fuchs, W., *Die Chemie des Lignins*, Berlin, 1926, pp. 243, 276.
567. Bailey, A. J., *Ind. Eng. Chem. Anal. Ed.* **8**, 389 (1936).
568. Beckmann, E., Liesche, O., and Lehmann, Fr., *Biochem. Z.* **139**, 502 (1923).
569. Schellenberg, H., *Jahrb. wiss. Botan.* **29**, 237 (1896); Nathansson, A., *Jahrb. wiss. Botan.* **32**, 671 (1898).
570. Phillips, M., and Goss, M. G., *J. Agr. Research* **51**, 301 (1935).
571. Cf. also Sherebow, *Papier-Fabr.* **25**, 47 (1937).
572. Tobler, F., *Ber.* **58**, 143 (1940).
573. Vanzetti, B. L., *Atti V Congr. nazl. chim. pura applicata, Rome 1935*, Pt. II, 932 (1936); *Chem. Zentr.* **1937**, **I**, 2192; cf. also *Chem. Zentr.* **1938**, **I**, 618.
574. Vanzetti, B. L., and Dreyfuss, P., *Gazz. chim. ital.* **64**, 381 (1934); Dreyfuss, P., *ibid.* **66**, 96 (1936).
575. Lindsey, J. B., and Tollens, B., *Ann.* **267**, 353 (1892).
576. Holmberg, B., *Svensk Kem. Tid.* **32**, 56 (1920); *Ber.* **54**, 2389, 2406 (1921).
577. Erdtman, H., *Ann.* **513**, 229 (1934); *Svensk Kem. Tid.* **48**, 250 (1936).
578. Haworth, R. D., and Sheldrick, G., *J. Chem. Soc.* **1935**, 636.
579. Keimatsu, S., Ishiguro, T., and Yamamoto, G., *Chem. Abstracts* **31**, 7439 (1937); cf. also Emde, H., and Schartner, H., *Naturwissenschaften* **22**, 743 (1934).
580. Hibbert, H., *Paper Trade J.* **113**, No. 4, 35 (1941).
581. Erdtman, H., *Ann.* **503**, 283 (1933); *Svensk Papperstidn.* **44**, 243 (1941).
582. Freudenberg, K., *Akad. Wiss., Heidelberg, Jahresheft 1942/43* (lecture given Jan. 9th, 1943); *Svensk Kem. Tid.* **55**, 201 (1943).
583. Freudenberg, K., and Richtzenhain, H., *Ber.* **76**, 997 (1943); Richtzenhain, H., *Ber.* **77**, 409 (1944).
- 583 a. Freudenberg, K., *Angewandte Chemie* **51**, 228 (1949); *Sitzungsber. d. Heidelberger Akad. d. Wissensch., Math.-naturwiss. Kl.* **1949**, 151; Freudenberg, K., and Heimberger, W., *Chem. Ber.* **83**, 519 (1950).
584. Kratzl, K., *Experientia* **4**, 110 (1948).
585. Klason, P., *Cellulosechemie* **10**, 113 (1932).
586. Klason, P., *Hauptversamlungsber. Ver. Zellstoff- u. Papier-Chemiker u. Ingenieure* **1908**, p. 52.
587. Freudenberg, K., and Ploetz, Th., *Ber.* **73**, 754 (1940); Ploetz, Th., *Cellulosechemie* **18**, 49 (1940).
588. Klason, P., *Cellulosechemie* **4**, 81 (1923); **12**, 36 (1931); *Ber.* **69**, 676 (1936).
589. Cf. Müller, O. A., and Storch, K., *Ber.* **72**, 73 (1939); Müller, O. A., and Bartholme, M., *Papier-Fabr.* **37**, 103 (1939); cf. also Larsson, A., *Svensk Papperstidn.* **46**, 93 (1943).

590. Häggglund, E., and Proffe, B., *Svensk Kem. Tid.* **45**, 117 (1933); Häggglund, E., and Bratt, L. C., *ibid.* **48**, 125 (1936); Häggglund, E., and Sävö, G., *Svensk Papperstidn.* **40**, 23 (1937).
591. Hilpert, R. S., and Littmann, E., *Ber.* **67**, 1551 (1934); Hilpert, R. S., *Cellulosechemie* **16**, 92 (1935).
592. Norman, A. G., *Biochem. J.* **31**, 1567 (1937).
- 592 a. Jensen, W., *Finnish Paper Timber J.* **31**, 143 (1949).
593. Noll, A., and Hölder, F., *Papier-Fabr.* **29**, 485 (1931); Noll, A., Bolz, F., and Fiedler, H., *Papier-Fabr.* **30**, 613 (1932); Noll, A., and Bolz, F., *Papier-Fabr.* **31**, 594 (1933).
594. Noll, A., Bolz, F., and Fiedler, F., *Papier-Fabr.* **30**, 613 (1932); **31**, 594 (1933).
595. Häggglund, E., and Giertz, H. W., *Svensk Papperstidn.* **45**, 129 (1942); see also Sieber, R., *Die chemisch-technischen Untersuchungsmethoden der Zellstoff- und Papierindustrie*, Berlin, 1943, p. 679.
596. Cohen, W. E., and Harris, E. E., *Ind. Eng. Chem. Anal. Ed.* **9**, 234 (1937); cf. Norman, A. G., and Jenkins, S. H., *Nature* **131**, 729 (1933); Campbell, W. G., and Bamford, K. F., *Biochem. J.* **30**, 419 (1936); Harris, E. E., and Mitchell, R. L., *Ind. Eng. Chem. Anal. Ed.* **11**, 153 (1939).
597. König, J., and Rump, E., *Z. Untersuch. Nahr.- u. Genussm.* **28**, 177 (1914); König, J., and Becker, E., *Z. angew. Chem.* **32**, 155 (1919); Schwalbe, C. G., and Becker, E., *Z. angew. Chem.* **32**, 128, 229 (1919); Mahood, S. A., and Cable, D. E., *Ind. Eng. Chem.* **14**, 933 (1922); Sieber, R., *Zellstoffchem. Abhandl.* **1**, 52 (1920); Sieber, R., and Rosenlund, P., *Zellstoff u. Papier* **2**, 251 (1922); Cleve-v. Euler, A., *Cellulosechemie* **4**, 109 (1923); Billington, P. S., Summonds, F. A., and Baird, P. K., *Paper Trade J.* **96**, No. 4, 30 (1933); Sieber, R., *Die chemisch-technischen Untersuchungsmethoden der Zellstoff- und Papierindustrie*, Berlin, 1943, p. 114ff.
598. Cf. Hilpert, R. S., *Ber.* **67**, 1337 (1934).
599. Krull, H., Dissertation, Danzig, 1916.
600. Eichler, O., *Cellulosechemie* **15**, 114 (1934); **16**, 1 (1935).
601. Klatt, W., *Angew. Chem.* **48**, 112 (1935).
602. Helferich, B., and Böttger, St., *Ann.* **476**, 150 (1929).
603. Fredenhagen, K., and Cadenbach, G., *Angew. Chem.* **46**, 113 (1933).
604. Wiechert, K., *Cellulosechemie* **18**, 57 (1940).
605. Ender, W., and Uebel, O., *Cellulosechemie* **17**, 104 (1936).
606. Hottenroth, V., German Pat. 306,818 (1918).
607. Willstätter, R., *Ber.* **55**, 2637 (1922).
608. Kalb, L., in: Klein, *Handbuch der Pflanzenanalyse*, Vienna, 1932, vol. II, p. 190.
609. Wenzl, H., *Papier-Fabr.* **22**, 105 (1924); **23**, 305 (1925).
610. König, J., and Becker, E., *Z. angew. Chem.* **32**, 155 (1919).
611. Ritter, G. J., *Ind. Eng. Chem.* **14**, 1050 (1922); **15**, 1264 (1923).
612. Kalb, L., cf. ref. 608, p. 201.
613. Cf. Häggglund, E., and Urban, H., *Biochem. Z.* **206**, 245 (1929).
614. Ritter, G. J., and Barbour, J. H., *Ind. Eng. Chem. Anal. Ed.* **7**, 238 (1935).
615. Waentig, P., and Kerenyi, E., *Zellstoffchem. Abhandl.* **1**, 65 (1920); *Papier-Fabr.* **18**, 920 (1920); Waentig, P., and Gierisch, W., *Z. angew. Chem.* **32**, 173 (1919).
616. Tingle, A., *Ind. Eng. Chem.* **14**, 40 (1922).
617. Kürschner, K., and Wittenberger, K., *Papier-Fabr.* **37**, 285, 297, 311 (1939).
618. Cf. Sabalitschka, T., and Dietrich, K. R., *Pharm. Z.* **69**, 425, 342 (1924).
619. Cross, C. F., Bevan, E. J., and Briggs, J. F., *Chem.-Ztg.* **31**, 725 (1907).

620. Votoček, E., and Potměšil, R., *Ber.* **49**, 1185 (1916).
621. Neumann, M., Dissertation, Brünn, 1925.
622. Fuchs, W., *Die Chemie des Lignins*, Berlin, 1926, p. 57.
623. Sieber, R., *Die chemisch-technischen Untersuchungsmethoden der Zellstoff- und Papierindustrie*, Berlin, 1943, p. 121ff.
624. Tschirch, A., and Stock, E., *Die Harze*, 3rd ed., Berlin, 1933-1935; Wiesner, J. v., *Die Rohstoffe der Pflanzenreiches*, vol. I, Leipzig and Berlin, 1914, p. 151ff; Meyer-Jacobson, *Lehrbuch der organischen Chemie*, vol. II, part 4, Berlin and Leipzig, 1924, p. 125ff.
625. Wiesner, J. v., *Die Rohstoffe des Pflanzenreiches*, vol. I, Leipzig and Berlin, 1914, p. 214.
626. Mayr, H., *Das Harz der Nadelhölzer*, Berlin, 1894, p. 81.
627. Klason, P., and Köhler, J., *Arkiv Kemi, Mineral. Geol.* **2**, No. 3, 19 (1904).
628. Bergström, H., *Om träkolning*, Stockholm, 1922, p. 33.
629. Austerweil, G., and Roth, J., *Gewinnung und Verarbeitung von Harz und Harzprodukten*, München, 1917.
630. Bergström, H., and Fagerlind, O., *Jernkontorets Ann. Proceedings* **9**, 90 (1908).
631. Aschan, O., *Ber.* **39**, 1447 (1906).
632. Bergström, H., *Jernkontorets Ann. Proceedings* **11**, 658, 725 (1910).
- 632 a. Semmler, F. W., and Schiller, H. v., *Ber.* **60**, 1591 (1927).
633. Cf. Hawley, L. F., and Wise, L. E., *The Chemistry of Wood*, New York, 1926, p. 112; Kurth, E. F., in Wise, L. E., *Wood Chemistry*, New York, 1946, p. 390.
634. Schorger, A. W., *Ind. Eng. Chem.* **5**, 971 (1913).
635. Schorger, A. W., *Forest Serv. Bull.* **119**, 18 (1913).
636. Schorger, A. W., *Ind. Eng. Chem.* **7**, 321 (1915).
637. Dupont, G., and Barraud, M., *Bull. inst. pin.* **1929**, 155.
638. Schorger, A. W., *J. Am. Chem. Soc.* **39**, 1040 (1917).
639. Thurber, F. H., and Roll, L. J., *Ind. Eng. Chem.* **19**, 739 (1927); Schorger, A. W., *ibid.* **6**, 631 (1914).
640. Arrhenius, O., *Svensk Botan. Tid.* **36**, 95 (1942).
641. Dahlén, A., Dissertation, Stockholm, 1943.
642. Bergström, H., *Jernkontorets Ann. Proceedings* **12**, 507 (1911).
643. Sandqvist, H., *Ing. Vetenskaps Akad. Handl.* No. **10** (1922).
644. Hasselström, T., *Finnish Paper Timber J.* **5**, 632 (1925).
- 644 a. Hibbert, H., and Phillips, S. B., *Can. J. Research* **4**, 1 (1931).
- 644 b. Kurth, E., *F. Ind. Eng. Chem.* **25**, 192 (1933).
645. Dittmer, M., *Z. angew. Chem.* **39**, 262 (1926).
646. Sandermann, W., *Cellulosechemie* **21**, 30 (1943).
647. Schwalbe, C. G., and Schulz, W., *Chem.-Ztg.* **42**, 229 (1918); *Z. angew. Chem.* **31**, 125 (1918).
648. Anderson, A. B., *Ind. Eng. Chem.* **38**, 759 (1946).
649. Richter, E., *Wochbl. Papierfabr.* **44**, 2486 (1913).
650. Schwalbe, C. G., and Grimm, H., *Wochbl. Papierfabr.* **44**, 3247 (1913).
651. Sieber, R., *Über das Harz der Nadelhölzer*, Berlin, 1925.
652. Wahlberg, H. E., *Papier-Fabr.* **20**, 1136 (1922).
653. Aschan, O., *Finska Kemistsamfundets Medd.* **5**, 4 (1918).
654. Klason, P., and Köhler, J., *Arkiv Kemi, Mineral. Geol.* **2**, No. 13 (1905).
655. Nordenskjöld, J., *Arkiv Kemi, Mineral. Geol.* **4**, No. 28, 9 (1912).
656. Cleve-v. Euler, A., *Cellulosechemie* **4**, 1 (1923).

657. Klason, P., *Cellulosechemie* **4**, 84 (1923).
658. Barnes, F., *Chem. Met. Eng.* **23**, 504 (1923).
659. Tschirch, A., and Stock, E., *Die Harze*, 3rd ed., Berlin, 1933-1935.
659. a. Harris, G. C., and Sanderson, T. F., *J. Am. Chem. Soc.* **70**, 2079, 2081 (1948).
660. Ruzicka, L., and Sternbach, L., *Helv. Chim. Acta* **23**, 124 (1940).
661. Fieser, L., and Campbell, W. P., *J. Am. Chem. Soc.* **60**, 159 (1938); Ruzicka, L., and Kaufmann, St., *Helv. Chim. Acta* **23**, 1346 (1940); **24**, 1425 (1941); Ruzicka, L., Sternbach, L., and Jeger, O., *ibid.* **24**, 504 (1941).
- 661 a. Harris, G. C., and Sanderson, T. F., *J. Am. Chem. Soc.* **70**, 334, 339 (1948).
662. Vesterberg, K. A., *Ber.* **36**, 4200 (1903).
663. Fleck, E., and Palkin, S., *J. Am. Chem. Soc.* **60**, 921, 2621 (1938); **62**, 2044 (1940).
664. Ruzicka, L., Bernold, E., and Tallichet, A., *Helv. Chim. Acta* **24**, 223 (1941); Ruzicka, L., Bernold, E., *ibid.* **24**, 931 (1941).
665. Brandt, C. W., and Neubauer, L. G., *J. Chem. Soc.* **1939**, 1031.
666. Cf. Enkvist, T., *Svensk Papperstidn.* **50**, 351, 363 (1947).
667. Pajari, K., *Ann. Acad. Sci. Fennicae* **59 A**, No. 6 (1942).
668. Wise, L. E., and Moore, S. T., *J. Org. Chem.* **10**, 516 (1945).
669. Erdtman, H., *Svensk Kem. Tid.* **48**, 250 (1936); *Svensk Papperstidn.* **42**, 115 (1939).
670. Haworth, R. D., *Ann. Repts. on Progress Chem. Soc., London* **33**, 267 (1937).
671. Schroeter, G., Lichtenstadt, L., and Irineu, D., *Ber.* **51**, 1587 (1918).
672. Briggs, L. H., Peak, D. A., and Woolloxall, J. L. D., *J. Proc. Roy. Soc. N. S. Wales* **69**, 61 (1935); Haworth, R. D., and Richardson, T., *J. Chem. Soc.* **1935**, 633.
673. Yoshiki, Y., and Ishiguro, T. J., *J. Pharm. Soc. Japan* **53**, 11 (1933); Keimatsu, S., and Ishiguro, T. J., *ibid.* **55**, 45 (1935).
674. Vanzetti, B. L., and Dreyfuss, P., *Gazz. chim. ital.* **64**, 381 (1934).
675. Briggs, L. H., and Frieberg, A. G., *J. Chem. Soc.* **1937**, 271.
676. Haworth, R. D., and Kelly, W., *J. Chem. Soc.* **1927**, 384.
677. Erdtman, H., *Svensk Kem. Tid.* **48**, 230, 236 (1936).
678. Robinson, R., and Smith, H. G., *J. Proc. Roy. Soc. N. S. Wales* **48**, 449 (1915).
- 678 a. Erdtman, H., *Ann.* **516**, 162 (1935).
679. Smith, H. G., *J. Proc. Roy. Soc. N. S. Wales* **46**, 187 (1912).
680. Birch, A. J., and Lions, F., *J. Proc. Roy. Soc. N. S. Wales* **71**, 391 (1935); Aulin-Erdtman, G., and Erdtman, H., *Svensk Papperstidn.* **47**, 22 (1944).
681. Erdtman, H., *Svensk Papperstidn.* **47**, 155 (1944).
682. Erdtman, H., *Svensk Papperstidn.* **46**, 226 (1943).
683. Brauns, F. E., *J. Org. Chem.* **10**, 216 (1945).
684. Pearl, J. A., *J. Org. Chem.* **10**, 219 (1945).
- 684 a. Lackey, H. B., Moyer, W. W., and Hearon, W. M., *Tappi* **32**, 469 (1949).
- 684 b. Fisher, G. D., Kyame, L., and Bickford, W. G., *J. Am. Oil Chemists' Soc.* **24**, 340 (1947).
- 684 c. Erdtman, H., and Lindberg, B., *Acta Chem. Scand.* **3**, 982 (1949).
685. Borsche, W., and Niemann, J., *Ann.* **499**, 59 (1932).
686. Aulin-Erdtman, G., and Erdtman, H., *Svensk Papperstidn.* **47**, 22 (1944).
687. Erdtman, H., *Svensk Papperstidn.* **42**, 115, 344 (1939).
688. Haworth, R. D., *J. Chem. Soc.* **1942**, 448.
689. Erdtman, H., *Ann.* **539**, 116 (1939).
690. Erdtman, H., and Rennerfelt, E., *Svensk Papperstidn.* **47**, 45 (1944); Erdtman, H., *ibid.* **48**, 217 (1945); *Svensk Kem. Tid.* **56**, 95 (1944).
691. Koch, J. E., and Krieg, W., *Chem.-Ztg.* **62**, 140 (1938).

692. Aulin-Erdtman, G., and Erdtman, H., *Ber.* **74**, 50 (1941); Späth, E., and Liebherr, F., *Ber.* **74**, 869 (1941); Späth, E., and Kvorup, K., *Ber.* **74**, 1424 (1941).
693. Cox, R. F. B., *J. Am. Chem. Soc.* **62**, 3512 (1940).
694. Anderson, A. B., and Sherrard, E. C., *J. Am. Chem. Soc.* **55**, 3813 (1933).
695. Erdtman, H., and Gripenberg, J., *Nature* **161**, 719 (1948); *Acta Chem. Scand.* **2**, 625 (1948); Gripenberg, J., *ibid.* **2**, 639 (1948); Anderson, A. B., and Gripenberg, J., *ibid.* **2**, 644 (1948).
696. Klason, P., and Edlund, T., *Arkiv Kemi, Mineral. Geol.* **2**, No. 12 (1905).
697. Czapek, F., *Biochemie der Pflanzen*, vol. III, Jena (1913), p. 510.
698. Benson, K. H., and Jones, F. M., *Ind. Eng. Chem.* **9**, 1096 (1917).
699. Scalione, C. C., and Merrill, D. R., *Ind. Eng. Chem.* **11**, 643 (1919).
700. Wilson, J. A., and Kern, E. J., *Ind. Eng. Chem.* **12**, 465, 1149 (1920); **13**, 772 (1921).
701. Forman, L. V., and Niemeyer, D. D., *TAPPI Monograph No. 4*, 167 (1947).
702. Zeisel, S., in Wiesner, J. v., *Die Rohstoffe des Pflanzenreiches*, 3rd ed., Leipzig, 1918, vol. II, p. 348.
- 702 a. Gnam, H., *Die Gerbstoffe und Gerbmittel*, 3rd ed., Stuttgart, 1949.
703. Erdtman, H., *Spensk Kem. Tid.* **56**, 6, 26-95 (1944). Cf. also Lindstedt, G., *Acta Chem. Scand.* **4**, 772 (1950).
- 703 a. Lindstedt, G., *Acta Chem. Scand.* **4**, 118 (1950), and 19 preceding papers.
704. Pew, I. C., *Tappi* **32**, 39 (1949).
705. Robinson, G. M., and Robinson, R., *J. Chem. Soc.* **1935**, 744.
706. Schwalbe, C. G., and Becker, E., *Z. angew. Chem.* **32**, 229 (1919).
707. Hartig, R., *Botan. Zeit.* **46**, 837 (1888).
708. Hoffmeister, W., after Czapek, F., *Biochemie der Pflanzen*, vol. I, Jena, 1913, p. 679.
709. Molle, Th., after Czapek, F., *Biochemie der Pflanzen*, vol. III, Jena, 1913, p. 228, 298.
710. Isenberg, I. H., Buchanan, M. A., and Wise, L. E., *Paper Ind. and Paper World* **28**, 816 (1946).
- 710 a. Erdtman, H., *Tappi* **32**, 305 (1949).
711. Zimmerman, H., *Z. angew. Chem.* **6**, 426 (1893).
712. Schroeder, H., after Czapek, F., *Biochemie der Pflanzen*, vol. II, Jena, 1913, p. 401.
713. Sacc, F., *Ann. chim. et phys.* [3] **25**, 223 (1849).
714. Daube, W., quoted by Schorger, A. W., *The Chemistry of Cellulose and Wood*, N. Y., 1926, p. 51.
715. Weber, R., *Botan. Centr.* **32**, 314 (1887).
716. Stiles, W., *Trace Elements in Plants and Animals*, London, 1946.
717. Cross, W. E., *Ber.* **43**, 1526 (1910); Klason, P., *Ber.* **53**, 1864 (1920); Schwalbe, C. G., and Becker, E., *Z. angew. Chem.* **33**, 15 (1920); Schorger, A. W., *The Chemistry of Cellulose and Wood*, N. Y., 1926, p. 104.
718. Dore, W. H., *Ind. Eng. Chem.* **12**, 475 (1920).
719. Sarkar, P. B., *Chem. Zentr.* **1935**, II, 2214.
720. Ritter, G. J., and Kurth, E. F., *Ind. Eng. Chem.* **25**, 1250 (1933); *J. Am. Chem. Soc.* **56**, 2720 (1934); Ritter, G. J., and Bird, C. D., *ibid.* **59**, 802 (1937).
721. Tang, Y. C., *Cellulosechemie* **16**, 90 (1935).
722. Klingstedt, F. W., *Finska Kemistsamfundets Medd.* **46**, 97 (1937).
723. Freudenberg, K., *Ann.* **433**, 230 (1923).
724. Klason, P., *Ing. Vetenskaps Akad. Handl.* No. **13** (1922).

725. Häggglund, E., Sandelin, O., Nyman, C., Eriksson, T., and Koskull, H. v., *Svensk Papperstidn.* **37**, 133 (1934); Häggglund, E., Ljunggren, S., Nihlén, H., and Sandelin, O., *ibid.* **38**, 454 (1935).
726. Klason, P., *Tek. Tid. Uppl. C. Kemi* **38**, 83 (1908).
727. König, J., and Becker, E., *Z. angew. Chem.* **32**, 155 (1919).
728. Schwalbe, C. G., and Becker, E., *Z. angew. Chem.* **32**, 229 (1919).
729. Schwalbe, C. G., *Z. angew. Chem.* **32**, 125 (1919).
730. Schwalbe, C. G., and Becker, E., *Z. angew. Chem.* **33**, 14 (1920).
731. Häggglund, E., and Johnson, T., *Zellstoff u. Papier* **7**, 49 (1927).
732. Schorger, A. W., *Ind. Eng. Chem.* **9**, 556 (1917).
733. Mahood, S. A., and Cable, D. E., *Ind. Eng. Chem.* **14**, 933 (1922).
734. Ritter, G. J., and Fleck, L. C., *Ind. Eng. Chem.* **14**, 1050 (1922).
735. Ritter, G. J., and Fleck, L. C., *Ind. Eng. Chem.* **15**, 1055 (1923); **18**, 608 (1926); cf. also Fréeman, R. D., and Petersen, F. C., *Ind. Eng. Chem. Anal. Ed.* **13**, 803 (1941).
736. Scharkow, W. I., and Muromzewa, W., *Chem. Zentr.* **1940**, **II**, 2109.
737. Häggglund, E., *Finnish Paper Timber J.* **4**, 444, 468 (1924).
738. Stockman, L., and Häggglund, E., *Svensk Papperstidn.* **51**, 269 (1948).
739. Staudinger, H., and Husemann, E., *Holz Roh- u. Werkstoff* **4**, 343 (1941).
740. Jayme, G., and Finck, F., *Cellulosechemie* **22**, 102 (1944).
741. Cross, W. E., and Tollens, B., *J. Landw.* **59**, 185 (1911).
742. Schorger, A. W., *Ind. Eng. Chem.* **9**, 556 (1917).
743. Häggglund, E., and Ljunggren, S., *Svensk Kem. Tid.* **45**, 123 (1933).
744. Kurth, E. F., *Chem. Revs.* **40**, 33 (1947).
- 744 a. *Northeastern Wood Utilization Council*, New Heaven, Bull. No. 25 (1949).
745. Trendelenburg, R., *Das Holz als Rohstoff*, Munich and Berlin, 1939, p. 100.
746. Dolmetsch, H., Franz, E., and Correns, E., *Kolloid-Z.* **106**, 176 (1944).
747. Schramek, W., and Stenzel, A., *Cellulosechemie* **19**, 93 (1941).
748. Cf. Höhnel, F. v., *Die Mikroskopie der technisch verwendeten Faserstoffe*, 2nd ed., Wien and Leipzig, 1905.
749. Lewis, H. F., and Richardson, C. A., *Paper Trade J.* **109**, No. 14, 28 (1939).
- 749 a. Häggglund, E., and Webjörn, B., *Svensk Papperstidn.* **52**, 171 (1949).
750. Steenberg, B., *Svensk Papperstidn.* **50**, No. 11B (Jubilee Vol. E. Häggglund), 155 (1947).
751. Kerr, T., and Bailey, I. W., *J. Arnold Arboretum (Harvard Univ.)* **15**, 327 (1934).
752. Farr, W. K., *J. Phys. Chem.* **42**, 1113 (1938).
753. Wiesner, J. v., *Sitzber. Akad. Wiss. Wien, Abt. I*, **93**, 17 (1886).
754. Dolmetsch, H., *Kolloid-Z.* **2**, 108, 183 (1944).
755. Lüdtke, M., *Ann.* **456**, 201 (1927); **466**, 27 (1928); *Biochem. Z.* **233**, 1 (1931) Hess, K., *Melliand Textilber.* **24**, 333 (1943).
756. Lauer, K., *Kolloid-Z.* **107**, 93 (1944).
757. Husemann, E., and Carnap, A., *J. makromol. Chem.* **1**, 16 (1943).
758. Hess, K., Kiessig, H., and Gundermann, J., *Z. physik. Chem.* **B49**, 64 (1941).

CHAPTER IV

THE DECOMPOSITION OF WOOD BY ACIDS. WOOD SACCHARIFICATION

I. Introduction

The utilization of the carbohydrates of wood as a raw material for sugar manufacture is a scientific, and especially a technical problem of more than 100 years' standing. Just as Kirchhoff's discovery in 1811 that starch could be transformed into sugar by heating with acids was epoch-making for starch chemistry, so was the observation made several years later in 1819 by Braconnot, that cellulose is transformed into sugar on treatment with concentrated sulfuric acid, of fundamental importance for the chemistry of cellulose. Extreme practical importance was attached to this discovery at that time, for it was thought that it would be possible in this way to carry out an economically feasible saccharification of cellulose. However, despite much work in this field, it has not yet been possible to achieve an economically practicable solution of the problem of wood saccharification by Braconnot's method.

Realizing the difficulty of converting wood to sugar economically with strong acid, Melsens in 1855 made the first attempt to carry out the conversion with dilute sulfuric acid at elevated temperatures and pressures.

Several investigators and inventors have worked along these lines right up to the most recent times, and the procedure has been repeatedly tested on a commercial scale. A single treatment of the wood, which was employed in these procedures, gave poor yields of sugar, and this might well be the reason why all attempts to achieve the saccharification of wood by this method have failed.

The idea of converting wood to sugar by heating with dilute acid was not given up, however. A new path was opened up by the procedure of H. Scholler, which is often called the Scholler-Tornesch process, after the town of Tornesch, where the first factory was erected. In contrast to the earlier procedures, this one involves complete digestion of the carbohydrates by

systematic extraction under pressure, so-called "pressure percolation." This process will be described in detail later on.

All procedures for the saccharification of wood with dilute mineral acids yield dilute sugar solutions, containing relatively great amounts of impurities, which makes the isolation of crystalline sugar economically impossible. At the present time, the solutions can be used only as fermentation substrates. Furthermore, the degree of saccharification obtained is less than that theoretically possible. Only by the use of strong hydrochloric acid has it thus far been possible to obtain a nearly quantitative conversion to sugar, and at the same time to isolate the sugar as such. It has required decades of work to perfect the technical details of this process—the so-called "Rheinau process," and to make the procedure economically feasible.

II. Saccharification with Hot Dilute Acids

G. F. Melsens (1) who was the first to saccharify wood with hot, dilute acid, treated the wood in an autoclave at about 180°C with 3-5% acid. However, experiments carried out in France on a technical scale were unsuccessful (2). A. Payen (3) hoped to obtain fermentable sugar along with paper pulp by using 10% hydrochloric acid. Bachel and Marchand (2) had, however, already proposed the use of dilute hydrochloric acid. W. Thorn (4) later reported that he had succeeded in this way in obtaining a yield of 18-25% of sugar. C. G. Zetterlund (5), working on a large scale, obtained 19% of fermentable sugar with five parts of 0.7% hydrochloric acid to one part of wood, and a reaction time of 8 hours at 0.1 atmospheres gage pressure.

A more thorough study of the saccharification of wood with dilute mineral acids was made by E. Simonsen (6), who investigated the effects of the strength of acid, the pressure, and the time of the reaction on the yield of sugar.

Simonsen concluded from his experiments that the following conditions gave the highest yield of sugar (about 22% of the weight of the wood for a single treatment): acid strength, 0.5%; pressure, 9 atm.; reaction time, 15 min. He also recommended that the quantity of acid be five times the weight of the wood, although the yield of sugar was not much affected if the quantity of acid was reduced to 2.5 times the weight of the wood. Simonsen believed that the cellulose was the sugar-forming constituent of the wood, because the yield of sugar was proportional to the cellulose content of the raw material.

By further hydrolysis of the unsaccharified residue less sugar was obtained than in the first saccharification, the yield amounting to only 13% of the original wood weight. Fermentation of the sugar solutions yielded about 6.5 l. of alcohol per 100 kg. of wood. On a technical scale the yield was less, amounting to only 2-6 l. per 100 kg.; this fact caused the operation of the factory to be suspended.

A. Classen (7) patented a series of procedures for wood saccharification, in which sulfurous acid was used as a hydrolyzing agent, either alone, or with the aid of such oxidizing agents as chlorine, oxygen, etc.

E. Reiferscheidt (8) carried out a series of experiments with a view to confirming the results of Simonsen and Classen, and obtained, in agreement with Simonsen, a yield of 6 l. of alcohol per 100 kg. of wood. [This result was also confirmed by Koerner (9)]. According to Classen, the best results with sulfurous acid were obtained when 9% acid was allowed to react for one hour at 140-150° C. Koerner (9) found that sulfurous acid did not give particularly good yields of sugar, and that oxidizing agents, with the exception of hydrogen peroxide, were harmful. Sulfurous acid was also used for a time by M. F. Ewen and G. H. Tomlinson (10), but they soon gave up this procedure, because of the difficulties involved, and later employed dilute sulfuric acid, like Simonsen (11).

Since the economic success of the saccharification with dilute acids is dependent on the quantities of water employed, i. e., on the relationship between the amount of acid and the amount of wood, E. Hägglund (12) investigated this matter more thoroughly. He found that decreasing the amount of acid to three times the quantity of wood did not affect the yield of fermentable sugar. Smaller quantities of liquid decreased the yield. The maximum yield per 100 kg. of dry wood corresponded to 8.7 l. of alcohol. The Classen sulfurous-acid procedure gave smaller amounts of fermentable sugar.

F. W. Kressman (13), following up the experiments of Simonsen, also determined the optimum conditions, and found the highest yields when the temperature was not raised above the point corresponding to a pressure of 7.5 atm. At the same time, the quantity of sulfuric acid was kept within the limits 1.8-2.5% of the weight of the wood, and the ratio of water to wood was 1.25 : 1.0. This last figure is not quite in agreement with the results of other investigators. Kressman also confirmed the fact that a rapid raising of the temperature (15-20 min.) and a short reaction time (15-20 min.) gave the best results. The yield of sugar and alcohol proved to be extremely dependent on the type of wood used, as may be seen from the following (abbreviated) table:

Type of Wood	Reducing Sugar in % of the Weight of Wood	Fermentable Sugar in % of the Total Sugar	Alcohol Yield in % of the Weight of Wood
Softwoods			
Western white pine.....	21.0	74.5	7.8
Red spruce.....	20.5	74.2	7.6
Red spruce.....	22.1	72.7	8.0
White pine.....	20.0	75.7	7.4
Longleaf pine.....	23.1	73.3	8.3
Longleaf pine.....	23.3	72.5	8.3
Lodgepole pine.....	21.9	67.4	7.2
Norway pine.....	25.6	66.9	7.7
Western larch.....	29.7	37.9	5.0
Western larch.....	30.5	57.9	8.7
Western larch.....	26.2	54.7	6.9
Western hemlock.....	21.2	77.6	7.6
Sugar pine.....	18.0	72.6	6.3
Sugar pine.....	20.2	66.5	7.1
White spruce.....	23.6	71.4	8.5
Douglas fir.....	21.1	67.4	6.8
Douglas fir.....	21.1	75.2	7.9
Hardwoods			
Birch.....	20.5	46.3	4.3
Sugar maple.....	18.9	34.0	3.0
Silver maple.....	20.7	47.2	4.7
Beech.....	21.2	22.2	2.0
White oak.....	17.3	50.5	4.1
Red oak.....	18.4	30.4	2.7
Sycamore.....	18.3	38.9	3.2
Slippery elm.....	16.6	26.8	1.4
Red gum.....	20.4	38.8	3.7
Cotton wood.....	18.2	32.9	2.4

Although the yield of reducing sugars from hardwood is not much smaller than that from softwood, the alcohol yield from the former is on the average less than half of that from the latter. This is due to the presence of large quantities of non-fermentable pentoses in the sugar from hardwood.

The poor fermentability of the sugar from "western larch" is attributable to the fact that this sugar is very rich in galactose, which is fermented only poorly or not at all by the strain of yeast used by Kressman (11). E. C. Sherrard (15), however, succeeded in fermenting galactose by using a Hungarian brewer's yeast, and thus raised the yield of alcohol to 10.8 g. per 100 g. of wood, with an average sugar yield of 29 g. Sherrard and G. W. Blanco (16) determined anew the optimum conditions for saccharification, and found the following for white spruce: 7.8 at. (175° C); 15 min. reaction time; 2.5% sulfuric acid (referred to the weight of the wood); 2 parts water to 1 part wood.

It has long been known that acetic and formic acids arise during the hydrolysis of wood (cf. p. 349). Sherrard and Blanco determined the quantity of acetic acid which is formed during the saccharification of

white spruce. By analyzing the residue, they further determined the amount of methyl alcohol split off, and the changes in the content of ash, cellulose, and pentosan.

According to their figures, 90% of the acetic acid, 80% of the pentosan, 30% of the cellulose, and 16% of the methoxyl are solubilized by the saccharification procedure. The lignin is evidently not dissolved.

Per Cent of the Weight of the Wood Before Hydrolysis

	Ether Extract- able	Acetic Acid on Hydro- lysis	CH ₃ O	Pento- san	Methyl- pento- san	Cellu- lose	Lig- nin	Ash
Before hydrolysis..	0.96	1.32	4.75	10.76	2.61	58.33	29.19	0.26
After hydrolysis...	1.08	0.116	3.99	1.79	3.06	39.67	29.63	0.06

W. P. Cohoe (17) thought that he could make the hydrolysis easier by a short pretreatment with steam. He also found that coarse sawdust was more suitable than fine.

Repeated attempts have been made to increase the yield of sugar by the addition of certain materials, which are alleged to have a catalytic effect.

As has been mentioned above, Classen attempted to convert sulfurous acid to sulfuric by the addition of oxidizing agents, with the evident hope of achieving an effect due to a "nascent" state. R. Gentzen and L. Roth (18) thought that they could conclude from their experiments that oxidizing agents had a favorable effect on the formation of sugar, even in the absence of sulfurous acid, but this conclusion is evidently wrong, to judge by later investigations (19). The problem has been studied particularly carefully by E. C. Sherrard and W. H. Gauger (19), who investigated a very large number both of organic and of inorganic materials, including ferric sulfate, copper sulfate, sodium bisulfite, zinc sulfate, potassium aluminium sulfate, nickel sulfate, manganous sulfate, cobalt sulfate, naphtholsulfonic acids, etc. In no case was an appreciable catalytic effect demonstrated; indeed most of the substances decreased the yield of alcohol.

A number of wood saccharification plants constructed in Germany during World War I used a modified Classen sulfurous-acid process. The modification consisted in the use of hydrochloric and sulfuric acids along with the sulfurous acid (20).¹ One to two per cent of SO₂ and HCl plus 3-4% of H₂SO₄, calculated on a dry weight basis, were added to a charge of 1,000 kg. of wood chips, and the temperature was raised rapidly to 165-170° C., corresponding to 7-8 atm. The hydrolysis was stopped after

¹ Voerkelius (21) could not detect any favourable result from adding sulfurous acid to a solution containing 0.2-2% of sulfuric acid at temperatures of 120-180° C.

20 minutes, and the contents of the digester were drawn off as rapidly as possible. The mass was extracted in diffusers, and yielded a 6-8% sugar solution. About 6-8 l. of alcohol were obtained per 100 kg. of dry wood in continuous operation.

Quite large quantities of unchanged carbohydrates remained in the residue, but it proved unprofitable to carry out repeated saccharifications.

The technique used here was obviously the same as that introduced much earlier in Georgetown by Ewen and Tomlinson. This procedure has been described by G. Foth (22) and especially by R. v. Demuth (23). Recently a summary has been given by E. C. Sherrard and F. W. Kressman (24). It was possible by appropriate procedure to obtain 6.4 l. of alcohol per 100 kg. of wood.

Certain by-products are formed during the saccharification of wood with dilute acid, and attempts have been made to recover them, in order to make the process more attractive economically (25). These products are acetic acid, methyl alcohol, acetone, aliphatic aldehydes, furfural, terpenes, and aromatic hydrocarbons, and part of them came over with the steam when the digester was blown off. The vapors were freed of acid constituents in a lime tower, and then condensed. The total amount of alcohols and aldehydes obtained on a technical scale was less than 1% of the weight of the wood. α -Pinene and *p*-cymene were found to be present in the terpene fraction, to the extent of 5% of the crude oil. Furfural was obtained from the condensate blown off from the digester. The yield was small—only 1% of the weight of the wood. Although the recovery of furfural was profitable, it was not sufficient to make the over-all production of alcohol from wood sugar economically practicable in peacetime, and the factories were shut down after the end of the war.

There are evidently several reasons, not all of them now known, why it is not possible to obtain more than 8-9 l. of alcohol (16-18% of fermentable sugars) from 100 kg. of wood by hydrolysis with hot, dilute mineral acids, although it should theoretically be possible to obtain about four times as much. It should be emphasized first of all, that the easily hydrolyzable carbohydrates which first become saccharified are rapidly decomposed by further cooking at the high temperatures used. It is true that the cellulose and the other wood polyoses yield further quantities of sugar, but under certain conditions the rate of sugar decomposition may become greater than the rate of hydrolysis. The decomposition has been shown to proceed faster in concentrated solutions than in dilute ones, so that it is advisable not to make the ratio of water to wood too small.

The ratio between the rates of the hydrolysis of cellulose and the decomposition of glucose, previously studied by H. Lüers (26), H. Scholler (27)

and F. Thiersch (28) (cf. p. 94), has recently been reinvestigated by J. F. Saeman (29) (cf. p. 397).

E. C. Sherrard and W. H. Gauger (19) attempted unsuccessfully to achieve a better yield by increasing the acid concentration from 5 to 30% H_2SO_4 , while keeping the other conditions unchanged (15 min. at 175°C) (16). Nearly all the cellulose in the wood went into solution when the sulfuric acid concentration was raised, to be sure, but the quantity of sugar nevertheless decreased, as the following figures show:

Grams H_2SO_4 per 100 g. Dry Wood	Per Cent of the Weight of the Wood			
	Total Reducing Sugar	Fermentable Sugars	Cellulose in Residue	Dissolved Cellulose
5	21.98	16.29	31.7	26.5
10	21.54	18.00	20.46	37.74
15	19.71	16.10	13.71	44.50
20	16.00	13.67	8.95	49.25
30	7.28	2.70	2.14	56.06

The gradual decrease in the quantities of sugar obtained by repeated hydrolysis of the residues from earlier treatments is shown in the following table by J. Neuman (9):

Experiment No.	Sugar %	Alcohol %	Actual Yield of Alcohol in % of the Theoretical	Comments
1	18.3	5.1	50	Ordinary saccharification with hydrochloric acid; 100 g. dry sawdust gave about 80 g. dry residue
2	16.4	7.2	100	Hydrolysis of the residue from No. 1, (0.5 % sulfuric acid for 15 min. at 175°C)
3	13.1	5.5	100	Same as No. 2, using residue from No. 2
4	12.9	6.3	100	Same as No. 2, using residue from No. 3

The idea of obtaining sugar from wood by the action of hot, dilute acids was not given up, however. H. Scholler (30) developed a method for saccharifying all of the carbohydrate of wood, which was based on his previous studies of the effect of reaction conditions on the saccharification of cellulose with dilute acid (27) (cf. p. 94).

The wood chips are brought to the cooking vessels (or percolators) by elevators and packed into them by steam pressure. Warm (170°C) 0.4% sulfuric acid is pumped through from top to bottom, and the heat of the sugar solution which is drawn off is used to pre-heat the acid. After a time a certain amount of the hydrolyzate is drawn off and an equal quantity of fresh acid is pumped in, thus preventing part of the sugar dissolved from being destroyed by the hot acid. The process is continued until all the carbohydrate of the wood has reacted. After neutralization the solution is used for fermentation or for the manufacture of yeast.

When soft woods were used, a 3-4% sugar solution was obtained. However, the sugar was by no means completely fermentable, for the yield of alcohol was approximately 1.2 l. of 100% alcohol per 100 l. of solution.

There is no doubt that all of the carbohydrate is dissolved by hydrolysis, for the residue corresponds to a normal yield of lignin, but an appreciable amount of the sugar formed is destroyed in the medium, so that the maximum yield of fermentable sugar from soft wood does not exceed about 40%, although the theory calls for about 66%. Accordingly, about 20 l. of pure alcohol are produced per 100 kg. of dry wood. The higher the concentration of sugar, the more it is degraded. However, it is more profitable to produce alcohol or yeast from a more concentrated sugar solution than from a dilute one, so that there is an optimum economic concentration for the over-all process—saccharification plus fermentation. This optimum lies at approximately $2\frac{1}{2}\%$ of fermentable sugar, i.e., at about the same sugar concentration as that found in the waste liquors from the sulfite pulping process.

A procedure developed by O. Ant-Wuorinen (31) is similar to that of Scholler in that a sort of percolation is employed. The percolation lasts for 40 minutes at 145-185°C, and a sulfurous acid solution containing 0.2-2% of SO_2 is used instead of dilute sulfuric acid. In this process, too, it is impossible to avoid the loss of sugar by decomposition, but the losses are obviously less than those caused by the use of 0.5% sulfuric acid. The use of the acid sugar solution to saccharify new wood (also considered by Scholler) which would constitute a sort of diffusion process, would hold out greater promise of success with the use of SO_2 solutions (32). However, the old rule that the higher the sugar concentration, the greater the decomposition of the sugar, holds here, too. Ant-Wuorinen gives the following figures for his pilot plant:

Sugar Concentration %	Total Yield of Sugar, in % of the Weight of the Wood (Pine)
1.7	54-55
3.4	52
6	45

A yield of 60 l. of alcohol per cubic meter (0.27 cords) of pine wood was obtained. This corresponds to something more than 21 l. per 100 kg. of wood, a yield which is not markedly higher than that obtained with the Scholler process.

The saccharification of wood for the purpose of obtaining alcohol by fermentation became technically important because of the great industrial demand for alcohol during the war years (1939-1945) especially in America.

In this connection J. F. Saeman (29) has measured the reaction velocity

for the hydrolysis of various American woods by dilute sulfuric acid at high temperatures, and investigated the speed of the decomposition of the sugar at the same time. It turned out, as previously had been shown for glucose (26), that the decomposition of all the types of sugars studied were first-order reactions. The activation energy of the decomposition of glucose was 32,800 cal. and did not depend on the acid concentration within the limits 0.4-1.6%. An increase of 10° in temperature between 170-190°C caused a 125% increase in the rate of decomposition. Doubling the acid concentration doubled the speed of decomposition. It was further found, in agreement with the results of Lüers (26) and Thiersch (28), that the hydrolysis of pure cellulose in the form of cotton or of wood which had been freed of wood polyoses by pre-hydrolysis was a reaction of the first order. Doubling the acid concentration in the range 0.4-1.6% increased the velocity of hydrolysis by about 150% at 170-190°C. A 10° temperature rise increased the hydrolysis rate 186% in this temperature range. From these data it is apparent that raising either the temperature or the concentration of acid results in a greater increase in the rate of hydrolysis of cellulose than in the rate of destruction of glucose. Hence, the efficiency of conversion of cellulose to reducing sugar is increased by increasing acid concentration and temperature.

R. H. Plow, J. F. Saeman, H. D. Turner, and E. C. Sherrard (33) have reported experiments made on a pilot-plant scale in spherical rotary digesters with a capacity of about 230 l. Repeated cookings of the residue yielded 19-23 l. of alcohol per 100 kg. of wood (Douglas fir), or just as much as saccharification in a stationary percolator. No fewer than 15 successive cookings were required, but the time for each was short, so that only about $2\frac{1}{2}$ hours were consumed in all. A sulfuric acid concentration of 0.25-0.6% was employed at 170-185°C, using a ratio of wood to liquid of 1:3.

This procedure naturally has only academic interest, since, among other things, the residue must be washed completely free of sugar between the cookings.

A modification of the old one-stage process led to an increase in the yield of alcohol from 8.5 to about 11.5 l. of 95% alcohol per 100 kg. of wood. This "modified American process" is characterized by the use of high temperature (185-190°C), a sulfuric acid concentration of 1-2%, and a wood to liquid ratio of 1:2. If the process is repeated three or four times, and the digester held at the maximum temperature for 3-6 minutes each time, as much as 29% of fermentable sugar (based on the weight of the wood) can be obtained, corresponding to 16.5 l. of 95% alcohol per 100 kg. of wood. The original "American process" is the Tomlinson method mentioned

above, in which, according to Kressman, 100 parts of wood, 125 of water, and 1.8-2.5 of H_2SO_4 are heated to 173°C for 30-40 min. by the direct application of steam.

In the so-called "Madison wood sugar process" (34) 0.5-0.6% H_2SO_4 at 180°C is allowed to flow through the charge of wood continuously, rather than in batches as in the Scholler process. The sugars produced are removed more rapidly, saccharification is accomplished in less time, and steam consumption is therefore lower than in the German process. Using Douglas fir sawmill wood waste, the reducing sugar obtained with a reaction time of 2.7-3 hours amounted to about 50% of the bark-free wood, and the sugar concentration in the hydrolyzates was about 5%. Fermentation resulted in a yield of 24.5 l. 95% ethanol per 100 kg. wood, compared with 21 l. obtained in the Scholler process with a reaction time of 13-20 hours.

Alcoholic fermentation of wood sugar solutions, obtained by hydrolysis of Douglas fir waste wood with dilute sulfuric acid, has been thoroughly studied by E. E. Harris and co-workers (35). They point out that in agreement with previous findings (36, 37) removal of furfural (for example by flashing the hydrolyzate after neutralization) aids to fermentation. They also found that fermentation is facilitated, if the wort is clarified with aluminium sulfate. It is probable that a lignin-like substance, which is otherwise deposited on the yeast cells, is removed by this procedure (38). The alcohol yield from hydrolyzates containing 5% sugar was about 40% of the total reducing substance.

Production of yeast from wood sugar has been investigated by H. Fink, R. Lechner and E. Heinisch (39, 40), who used hydrolyzates from both the Scholler and Rheinau processes. *Torula utilis*, which ferments both hexoses and pentoses, and requires only ammonia as a source of nitrogen, was obtained in a yield of 40% of the total reducing sugars present in the wort. The high nutritive value of torula fodder yeast, especially as a source of protein and vitamins, has been pointed out by several authors (41). W. H. Peterson, J. F. Snell and W. C. Frazier (42) have also examined the conditions for a successful aerobic fermentation of wood hydrolyzates with torula yeasts, and found that an appropriate clarification and detoxification of the solutions is as necessary as in alcoholic fermentation (35). Hydrolyzates from different wood species, especially Douglas fir, spruce and Southern yellow pine, were investigated. The yeast yields (dry) obtained ranged between 35 and 42% of the total reducing sugar.

The suitability of wood hydrolyzates for the production of butanol and acetone by *Clostridium acetobutylicum* and of 2,3-butyleneglycol by *Acrobacter aerogenes* has been studied by E. E. Harris, E. Beglinger, G. J. Hajny and E. C. Sherrard (43).

In the wood saccharification process, as outlined above, a lignin residue is obtained, for which no satisfactory use has yet been found. Lignin from the Scholler process has been used for soil improvement and its conversion into plastics has been attempted, but evidently with only little success (40, 41). A process consisting of a partial hydrolysis of wood, especially hard wood wastes, has been developed by Sherrard and his co-workers at the U. S. Forest Products Laboratory (45) with the purpose of obtaining lignocellulose residues suitable for plastic molding. The hydrolytic action in this process is confined chiefly to a dissolution of the hemicelluloses, and the resulting lignin-enriched residue shows some plastic flow, which makes it suitable for pressure molding, especially after incorporation of "plasticizing" agents such as aniline or furfural. A similar process, working continuously, has been developed by R. Katzen and D. F. Othmer (46). It has been shown (47) that the lignocellulose material obtained in this process contains about 55% lignin, part of which is soluble in organic solvents. Methanol dissolved 36%, dioxane 38%, and glycol monomethyl ether, 60% of the total lignin present. R. Katzen and co-workers (48) have also examined the possibilities of obtaining furfural and organic acids by heating the hydrolyzates at a pressure of 100 pounds per square inch for 15 minutes and then extracting with high-boiling solvents.

III. Saccharification with Concentrated Mineral Acids

A. SULFURIC ACID

In connection with his attempts to saccharify cellulose, H. Braconnot (49) also investigated the behavior of wood toward concentrated sulfuric acid, and found that large quantities of sugar were formed. Braconnot used a large excess of sulfuric acid, which naturally precluded any possibility of making the process economically practicable. The extent of saccharification was determined by means of the Flechsig method (50) by G. A. Voerkelius (21). He used seven parts of 70% sulfuric acid to one part of wood, and obtained 67% of sugar, 70% of which was fermentable. This gave 24.8 g. of alcohol per 100 g. of dry wood. The saccharification was evidently complete, since the lignin residue from the same amount of wood was 30 g.

It had been recognized even before this that economic practicability was out of the question unless the quantity of sulfuric acid could be reduced without reducing the yield of sugar. Experiments along this line were undertaken by J. E. Arnould (51), who used 100 parts of sawdust to 110 parts of concentrated sulfuric acid. His report that 80-90% of the wood was converted into soluble material is either wrong, or is due to the fact that too concentrated acid was used. A. Classen (52) found that high

pressure could initiate an exothermic reaction in a mixture of one part of sawdust and $\frac{3}{4}$ parts of sulfuric acid of 57° B \acute{e} . Treatment of the mass with hot water resulted in the conversion of up to 60% of the wood to sugar. G. Ekström (53) also attempted to saccharify sugar with small quantities of strong sulfuric acid, both at low temperatures and at a temperature of 80°C.

E. Hägglund (12) determined the yields of sugar from sawdust and 70% sulfuric acid at various temperatures and with various reaction times. When the quantity of 70% sulfuric acid used was 100% of the weight of the wood, approximately 55% of sugar could be obtained at ordinary temperature.

These questions have recently been reinvestigated and large scale experiments have been carried out (54). It was found that quite good yields of sugar could be obtained with small amounts of acid, provided that the wood was used in a sufficiently finely divided form. Using a wood:acid ratio of 2:1 the sugar yield was 56% of the wood substance. The residue amounted to 35%, proving that only a small amount of unsaccharified material remains. Fermentation produced 48 l. of alcohol per 100 kg. of sugar.

It will be noted that the weight of sulfuric acid consumed is somewhat less than that of the sugar produced.

Low viscosity sulfite pulp ("fodder cellulose") could also be converted to sugar with a small amount of sulfuric acid. In a special experiment, for every 1.185 kg. "fodder cellulose," corresponding to 1 kg. dry pulp, 0.94 kg. concentrated sulfuric acid was used, the final concentration of the acid thus being about 80%. The sugar yield was 0.9 kg., which corresponded to about 90% yield, when the carbohydrate content of the pulp was taken into consideration. Since the sulfite pulping can be carried out in such a way that losses of sugar can be kept low, there is here a possibility of practically completely saccharifying the carbohydrates of the wood.

M. Giordani (55) believed that before saccharification with strong sulfuric acid could be made to occur economically it would be necessary to remove the wood polyoses and to degrade the cellulose completely to a "hydrocellulose" by pre-hydrolysis with 0.5-5% sulfuric acid at 135-150°C. However, this is by no means necessary, as has been shown above.¹

Even if it seems possible to obtain a quantitative yield of sugar from wood, it would entail the consumption of a considerable quantity of

¹ For other methods, see K. Mitterbiller-Epp (56). He pulps with 50% sulfuric acid, and precipitates the dissolved carbohydrates with water. The products so obtained are said to be suitable for fodder. Since these are cellulose dextrins, they can be fed only to animals which digest cellulose. Such animals can also digest pulp itself, which would be simpler.

sulfuric acid, and an equivalent amount of lime, since the solution has to be diluted, heated, and then neutralized with lime or chalk to remove the sulfuric acid, which precipitates as calcium sulfate. If the calcium sulfate is not utilized, it accumulates in huge quantities. It would undoubtedly be possible to reconvert it to sulfuric acid, but this would not be profitable except on a very large scale—far exceeding that of any imaginable factory for the saccharification of wood.

For the sake of completeness, it may be mentioned that the recovery of the sulfuric acid by dialysis through a copper ferrocyanide membrane has been proposed (57). This method would hardly be of any more value than a previous attempt to utilize the sulfuric acid of the hydrolysis solution for the preparation of soluble phosphates. The Th. Goldschmidt Co. procedure for recovering the acid in the form of hydrogen sulfide is out of the question, and it is also impossible to effect the recovery by electrolysis (58).

B. HYDROCHLORIC ACID

A. Béchamp (59) discovered as early as 1856 that fuming hydrochloric acid dissolved cellulose, and that sugar appeared in the solution after some time. The conditions for the formation of sugar were not precisely given, and Béchamp made no attempt to make a technical application of these important findings. In the eighties, however, E. S. Dangevilliers (60) reported a procedure for saccharifying wood with strong hydrochloric acid. He passed hydrogen chloride into moist sawdust until complete conversion to sugar had occurred. The excess hydrogen chloride was pumped off in a vacuum, and the mass treated with water and cooked, in order to complete the hydrolysis of the dissolved carbohydrates. The equipment used is fully described in the patent. It was impossible to recover the hydrochloric acid in this procedure, because of faulty arrangements for the heat transfer during the evaporation, and especially because of unsuitable equipment for the saccharification.

R. Willstätter and L. Zechmeister (61) in 1913 gave exact data as to the strength of hydrochloric acid required to achieve smooth dissolution and saccharification of cellulose. Willstätter patented the preparation of cellulose solutions. According to this patent, one part of sawdust is treated with seven parts of acid of specific gravity 1.209-1.213 (at 15° C., corresponding to 40-41% hydrochloric acid). After one hour the lignin is filtered off and the cellulose precipitated from the solution with water, salt solution, or alcohol. No mention of the extent of saccharification is made in the patent, but in the article by Willstätter and Zechmeister there are some

statements to the effect that complete saccharification of cellulose is possible only with a very great excess of hydrochloric acid. The dissolving power of the acid increased with its strength, but even 41% hydrochloric acid can give only a 15% solution of cellulose.

This slight dissolving power of concentrated hydrochloric acid compared with that of concentrated sulfuric acid is indeed a great disadvantage in the technical conversion of wood to sugar. While it is possible to effect complete saccharification with equal parts of concentrated sulfuric acid and wood, equal quantities of 40% hydrochloric acid and of wood give at most 21.6% of sugar, and this yield is achieved only after 24 hours. The time could be cut to 4 hours if the temperature was kept at 40°C., but prolongation of the reaction time did not increase the yield above 23.5%. With larger quantities of hydrochloric acid, the yield of sugar increased slowly, as the following figures show (62):

Relative Amount of Hydrochloric Acid, by Volume	Yield of Sugar, in % of Weight of the Wood, at 15° C
1	21.6
2	30.0
3	44.4
4	54.5
5	61.4
6	66.5
7	67.2

The yield could be increased only slightly by intimate mixing, kneading etc.; nor was any greater improvement noted when very fine sawdust was used.

When the excess of acid was kept as small as possible, i.e., when the concentration of the carbohydrate in solution was high, there occurred a strong reversion of the sugar first formed. Hence the advantage ascribed by Willstätter to the hydrochloric acid process over that with sulfuric acid, namely, that the hydrolysis could be followed polarimetrically from start to finish, is only a limited one. The polarimetric measurements, according to Willstätter, are best made on solutions which are quite dilute with respect to sugar.

The saccharification with hydrochloric acid, like that with sulfuric acid, must be considered as a two-stage process: solution in concentrated acid, and hydrolysis with dilute acid. H. Ost (63) has called attention to this fact.

The initial reactions occurring between cellulose and hydrogen chloride in the absence and in the presence of water have been studied by Schlubaeh and by Hess and their co-workers. Their results have been discussed in Chapter III (p. 101).

Willstätter's process leads to solutions which contain at most 3-4% of

sugar. It is unthinkable that the problem of converting wood to sugar could be solved in this way, for in the first place, solutions high in hydrogen chloride can not be evaporated in technical operation, and in the second place, even if it were possible to separate the sugar from the hydrochloric acid in this way it would still be uneconomical at such low concentrations of sugar.

A discovery essential for the development of the process was that of E. Hägglund, who found that hydrochloric acid solutions which showed no more dissolving power regained their activity when brought into contact with fresh sawdust. The saccharification stopped again when a certain quantity of carbohydrate had gone into solution; a new "equilibrium" had been established. The solution could then again take up carbohydrate from fresh sawdust. In this way it proved possible to obtain simultaneously both complete saccharification and concentrated sugar solutions, containing 30 g. of sugar or more per 100 cc. of solution. When the concentrated sugar solutions had been obtained in this way, the possibility arose of carrying out on a technical scale the separation of the acid from the sugar by vacuum distillation, and of doing it economically. This presupposes, however, that the sugar is stable enough to permit the solution to be heated to the temperature necessary for the distillation at the vacuum technically obtainable. The sugar solutions could actually be heated to 70°C without being decomposed in the time necessary for the distillation. So high a temperature is not necessary in practice.

Repeated saccharification in several successive reaction vessels and recovery of the hydrochloric acid by vacuum distillation of the sugar solutions are characteristic of the Rheinau process. The principles of this process were patented as long ago as 1917 (64), but it required a great deal of courage to put the principles into practice, for it could be foreseen that the most serious difficulties would arise in perfecting the apparatus for such a process.

The technical details of the process can not be discussed here. The difficulties connected with the apparatus were overcome in the course of many years. A large number of chemists and engineers have made significant contributions to the development of the process (65, 66). The essential steps of the process are shown schematically in Fig. 65.

The wood, consisting of any waste wood (or firewood) is shredded into pieces somewhat larger than the particles of ordinary sawdust, and dried to 5-10 per cent water content in a revolving drum, which is heated by means of the stack gases of the boiler plant. The dried wood is conveyed to the diffusion battery, which consists of a series of iron containers equipped with acid-proof linings.

A countercurrent system is used in the hydrolysis. The dried wood is mixed in the first diffuser with an acid-sugar solution which already has passed through the preceding diffusers. The fresh acid containing 40 per cent hydrogen chloride is brought into contact with a charge, which is already practically completely saccharified and extracted. It then proceeds

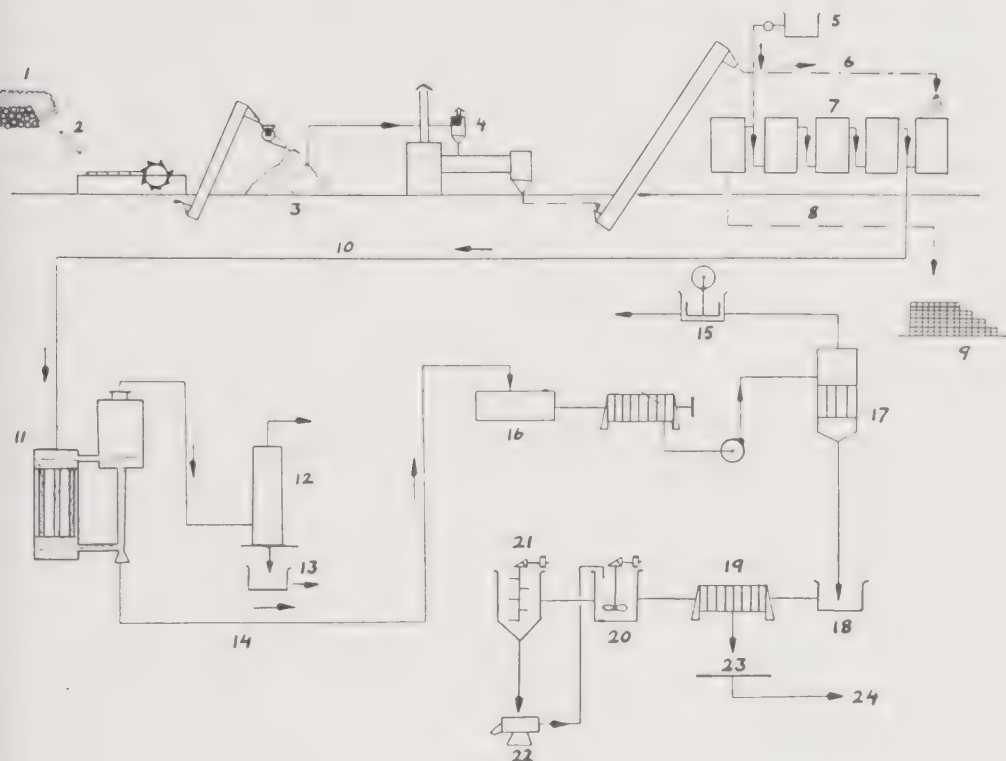


Fig. 65. Flow Diagram of the Rheinau Process.

- | | | |
|-------------------------------|--------------------------------------|------------------------------------|
| 1. Wood supply | Evaporation steps: | 17. Evaporator |
| 2. Wood shredder | 10. Sugar solution | 18. First crystallization |
| 3. Chips | 11. Evaporator for hydrochloric acid | 19. Filter press |
| 4. Wood dryer | 12. Condenser | 20. Solution vat |
| Saccharification steps: | 13. Hydrochloric acid | 21. Recrystallization |
| 5. Hydrochloric acid | 14. Sirup | 22. Centrifuge for pure crystals |
| 6. Dried wood chips | Crystallization steps: | 23. Sirup filtrate (mother liquor) |
| 7. Diffusion battery | 15. Vacuum pump | 24. To alcohol (by fermentation) |
| 8. Lignin | 16. Inversion | |
| 9. Lignin-briquetting process | | |

through the battery, successively meeting charges with increasing carbohydrate content and taking up more and more sugar. Finally, when it has been in contact with the fresh wood for a time, it is drawn off, and then contains about 32 per cent by volume of reducing sugar. From the last diffuser practically carbohydrate-free lignin is obtained, which is freed of hydrochloric acid by systematic washing. It can be briquetted without a binder and used as fuel or converted into charcoal. The use of the lignin residue in thermosetting plastics has also been proposed (67).

So far, however, there has evidently been no significant utilization of this lignin (40).

The operation may be explained as follows: We assume that the acid-sugar solution in one diffuser is in equilibrium with wood which still contains undissolved carbohydrate. Acid with a higher HCl content, coming from the preceding diffuser, displaces this solution into the next diffuser, which contains wood with a higher carbohydrate content. If this process is carried out systematically, the sugar content of the solution rises from one diffuser to the next, as is shown in Fig. 66. The curve is not linear; this fact shows clearly that the last traces of cellulose are not easily converted into sugar.

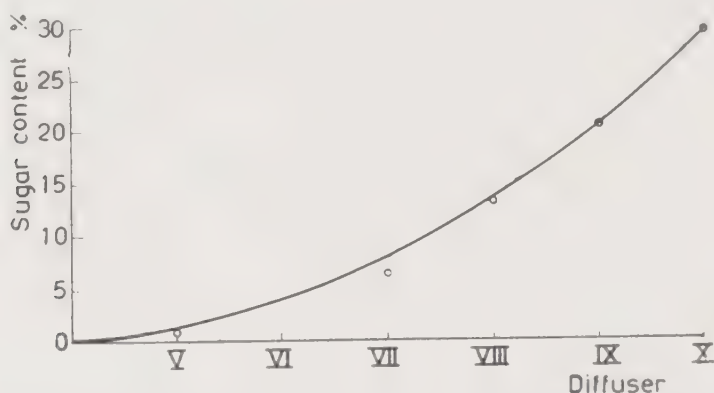


Fig. 66. Sugar content of the hydrochloric acid solutions in the various diffusers.

The sugar concentration of the final solution is dependent primarily on the number of the diffusers; Fig. 66 shows that seven diffusers would be required to achieve a concentration of 30%, at temperatures of 15-20°. (It should be noted that the "percentages" used here mean grams of sugar per 100 cc. of solution.) The discovery (68) that the quantity of hydrogen chloride decreased as that of sugar increased was also significant. The ratio of HCl to $(\text{HCl} - \text{H}_2\text{O})$, which was initially about 40% had decreased to about 32% in the last diffuser. This behavior may be attributed to the absorption of hydrogen chloride by the lignin. The relationship between the concentrations of sugar and hydrogen chloride are illustrated in Fig. 67.

A study of the processes in the diffusion battery gives the impression that there must exist an equilibrium involving the sugar content of the solvent and the carbohydrate content of the residue. This would be difficult to understand, however. The controlling factor is the concentration of the hydrochloric acid. An increase in the HCl content of the sugar solution increases the extent of saccharification and accelerates the process (68).

A reversion of the sugar occurs along with the saccharification, the extent of the reversion increasing with the sugar concentration. Apparently, the reversion proceeds to a mixture of oligosaccharides, mainly containing

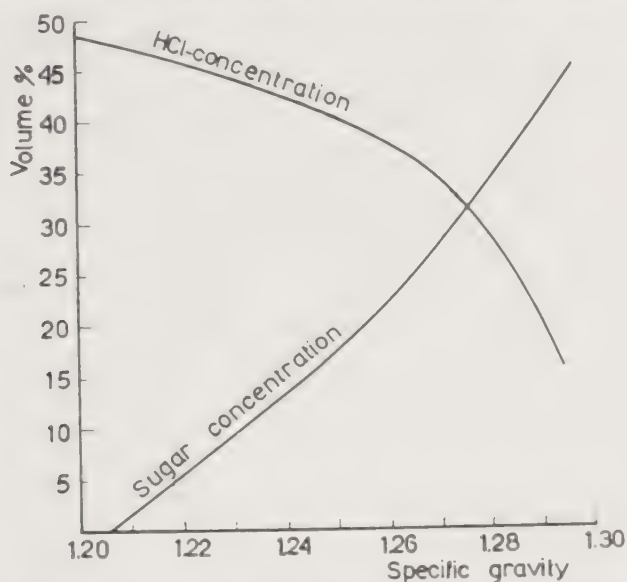


Fig. 67. Relationship between the hydrogen chloride and the sugar concentrations in saccharification solutions of different specific weight.

more than two monosaccharide units. The connection between the sugar concentration and the amount of reversion products may be seen from the following figures:

Per cent of carbohydrate in solution (calcd. as glucose)	7.6	15.6	32.2	46.6
Per cent of carbohydrate present as reversion product	26.6	32.5	47.1	54.2

After inversion, the sugar obtained from fir and pine (in yields of 65-70% of the wood) had the following composition:

	%
Glucose.....	61.9
Mannose.....	24.7
Galactose.....	4.0
Fructose.....	1.4
Xylose.....	8.0
	<hr/> 100.0

The sugar solution obtained from the battery is distilled under vacuum. Distillation is carried out by indirect steam heating and with rapid agitation of the solutions. The evaporators are equipped with tubes of a special acid-proof material of good heat conductivity. The hydrochloric acid is condensed and re-used in the hydrolysis step.

To separate the hydrochloric acid as far as possible, steam is blown into the concentrate at the end of the vacuum distillation. A sirup, consisting of sugars and their reversion products (see above, p. 407) is thus obtained.

It contains only about 3% of HCl, calculated on the amount of sugar present.

If the sugar is to be used for fermentation or for the production of crystalline sugar, the reversion products have to be inverted. For this purpose the raw hydrolyzate, which still is slightly acid, is diluted by three times its volume of water and heated for about half an hour at 120°C. The speed of inversion in 10% sugar solutions with 1% of HCl is shown in Fig. 68. The ordinate represents the inversion factor I , defined by:

$$I = \frac{(a - b) 100}{a},$$

where a is the glucose content when the inversion is complete, and b the glucose content at any given time.

Neutralization and con-

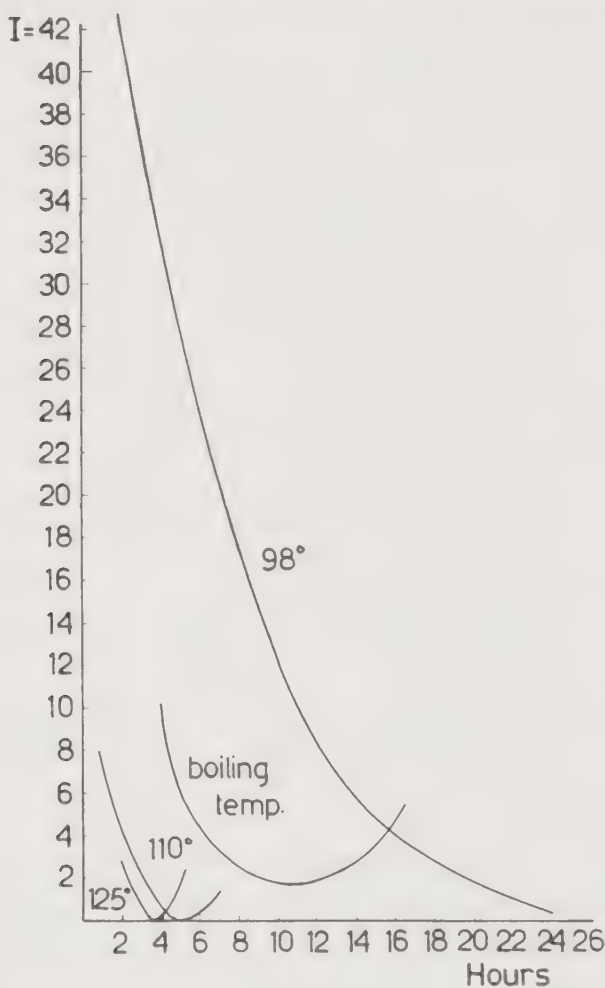


Fig. 68. The speed of hydrolysis of crude wood sugar at various temperatures.

centration yield crystalline sugar which can be used as fodder. The remaining molasses may be utilized in fermentation processes.

The suggestion has been made (69) that the hydrochloric acid could be removed by systematic dialysis instead of by distillation. However, there are no technically applicable membranes which will permit such a separation without the loss of excessive quantities of sugar from solutions containing large amounts of monosaccharides. It should also be emphasized that the hydrochloric acid recovered by dialysis would in any case be a dilute solution which would be of no value for the further operations.

In the past 10 or 20 years repeated attempts have been made to solve

the saccharification problem by the method of Dangevilliers, too. A. Wohl and H. Krull (70) immersed 5 g. of wood in 15 cc. of water, and saturated the mixture with hydrogen chloride. After 5 hours of hydrolysis, the hydrochloric acid was distilled off in a vacuum, leaving behind only small amounts of HCl. The mass was diluted with water to a volume of 100 cc., cooked for 8 hours, neutralized, treated with yeast nutrients, and fermented. The following results were obtained:

Raw Material	Sugar %	Alcohol %	Yield of Alcohol in % of the Theoretical (Calculated on Basis of Sugar)
Cotton.....	94.4-97.9	44.3-46.6	90.7-91.7
Mechanical pulp.....	62.65	15.48	50.0
Unbleached sulfite pulp.....	84.9	29.0	68.6
Unbleached soda pulp.....	88.7	25.3	60.0
Spruce wood.....	59.3-62.6	17.2-18.8	60.0-61.5
Rye straw.....	59.4-59.6	6.8-7.1	23.0-30.0

This process is out of the question for technical operation because of the heat developed when the hydrogen chloride is absorbed. In order to reduce this heat as much as possible, it has been suggested (71) that the wood be immersed not in water or in dilute HCl, but in 40% HCl, and that HCl gas then be led in until saturation is reached.

Nearly quantitative solution was obtained when the amount of hydrogen chloride was 80% of the weight of the wood. According to the patent, not only sugars, but also hydrolyzable dextrans are obtained. When the saccharification is complete, part of the hydrogen chloride is recovered by evacuation.

The Swiss chemists H. Terisse and M. Levy (72) used a method which is the same in principle as that described above. Dry sawdust was mixed with an equal weight of 10% hydrochloric acid, and the temperature was kept down to 25 C by cooling. The concentration of hydrochloric acid was then increased by passing in a quantity of gas equal to 10-20% of the weight of the wood. This can be done because of the adsorption of HCl by the wood. It must also be noted here that heat is developed, and must be removed. The inventors of the process attempted to do this by water cooling, using an apparatus similar to a mechanical roasting oven. The plates were hollow, and water circulated through them, cold in the upper part, and hot in the lower. The wood was kept in motion by stirring, and was conveyed from top to bottom, while the HCl gas streamed through in the opposite direction. Excess hydrogen chloride was driven off with hot air in another oven which was similarly constructed. The yield from this process was, however, so poor that it was necessary to close down the plant. With this failure, the solution of the problem of wood saccharifi-

cation according to the Dangevilliers' principle may well be considered to have been proved impossible.

J. W. Darboven (73) has proposed another solution to the problem of heat removal during the solution of hydrogen chloride. According to his method, the saccharification occurs in a solution of hydrogen chloride in an organic solvent. After the saccharification, the hydrogen chloride and the organic solvent are removed by heating, and the sugar is extracted from the residue. As yet, this process seems not to have been carried out on a commercial scale.

Many inventors have made proposals for increasing the yield of sugar and of shortening the reaction time. Wohl and Krull investigated the possible advantages of a pretreatment with chlorine. The reducing power of the product increased, to be sure, but this did not indicate an increased yield of sugar, but rather a decreased yield of alcohol. Treatment with sodium hydroxide, with or without the addition of chlorine, proved equally valueless.

A. Classen (74) has suggested improving the hydrolysis with hydrochloric acid by the use of certain catalysts, but tests have shown that the materials proposed have no noticeable effect.

C. OTHER PROCEDURES WITH CONCENTRATED ACIDS

The use of mixtures of concentrated acids instead of sulfuric or hydrochloric acid alone has been repeatedly proposed for digesting wood. It has already been mentioned that mixtures of hydrochloric and phosphoric acids are used to dissolve carbohydrates in the isolation of lignin.

Such a mixture was first proposed by R. Langhans (75), who also used mixtures of hydrochloric and sulfuric acids. These saccharification mixtures were patented by the Waldhof Cellulose Works and V. Hottenroth (57), Z. Ostenberg (76), and others. So far as is known, these mixtures were never used in pilot plant operations. Procedures in which hydrochloric acid is mixed with dehydrating agents, like zinc chloride (77) have also had no practical value thus far.

As has already been mentioned in another connection (cf. p. 101), K. Fredenhagen and G. Cadenbach (78), inspired by the experiments of B. Helferich, have converted cellulose to sugar with hydrogen fluoride. Hydrogen fluoride from fluorite and sulfuric acid is led over dry, finely divided wood, and is adsorbed. About 1 kg. of hydrogen fluoride is used per kg. of dry wood. After the digestion, the hydrogen fluoride can be recovered by pumping it off (79).

So far as is known, the procedure has had no practical results, chiefly,

no doubt, because the problem of designing suitable apparatus has been extremely difficult. Lüers (80), however, has reported that H. Hoch and H. Bohunek have succeeded in saccharifying wood in an economically practicable way with hydrogen fluoride (81). No factory is known to have been erected yet, however.

H. H. Schlubach's procedure (82) with 100% hydrochloric acid (cf. p. 101) has also not yet proved adaptable to technical operations.

A detailed description of German activities in the field of wood saccharification has been given by J. F. Saeman, E. G. Locke and G. K. Dickerman (40). For a recent review on wood saccharification see also E. E. Harris (83).

REFERENCES

1. Melsens, G. F., *Dinglers Polytech. J.* **138**, 426 (1856).
2. Pelouze, M. F., *Dinglers Polytech. J.* **150**, 394 (1859); cf. also *Compt. rend.* **48**, 327 (1859).
3. Payen, A., *Dinglers Polytech. J.* **185**, 308 (1867).
4. Thorn, W., *Dinglers Polytech. J.* **210**, 24 (1873).
5. Zetterlund, C. G., *Wagners Jahrbuch* **18**, 597 (1872).
6. Simonsen, E., *Z. angew. Chem.* **11**, 195, 219, 962, 1007 (1898).
7. Classen, A., German Pat. 118,540, 118,542-44 (1899); 130,980 (1901).
8. Reiferscheidt, E., *Z. angew. Chem.* **18**, 44 (1905).
9. Koerner, T., *Z. angew. Chem.* **21**, 2353 (1908); Neuman, J., Dissertation, Dresden, 1910.
10. Ewen, M. F., and Tomlinson, G. H., U.S. Pat. 763,472; *Chem.-Ztg.* **23**, 659 (1909).
11. Cf. Demuth, R. v., *Z. angew. Chem.* **26**, 786 (1913); U. S. Pat. 1,032,392, 1,032,440, 1,032,443, 1,032,444, 1,032,446-50 (1912).
12. Hägglund, E., *J. prakt. Chem.* [2] **91**, 358 (1915).
13. Kressman, F. W., *Ind. Eng. Chem.* **6**, 625 (1914); **7**, 920 (1915).
14. Cf. Schorger, A. W., *Ind. Eng. Chem.* **8**, 494 (1916).
15. Sherrard, E. C., *Ind. Eng. Chem.* **14**, 948 (1922).
16. Sherrard, E. C., and Blanco, G. W., *Ind. Eng. Chem.* **15**, 611 (1923).
17. Cohoe, W. P., U. S. Pat. 985,725 (1911); 985,726 (1911); *J. Soc. Chem. Ind. (London)* **31**, 513 (1912).
18. Gentzen, R., and Roth, L., German Pat. 147,844 (1901).
19. Koerner, T., *Z. angew. Chem.* **21**, 2353 (1908); Krull, H., Dissertation, Danzig, 1916; Sherrard, E. C., and Gauger, W. H., *Ind. Eng. Chem.* **15**, 63, 1164 (1923).
20. Heuser, E., *Cellulosechemie* **1**, 41 (1920).
21. Voerkelius, G. A., *Wochbl. Papierfabrik.* **42**, 852 (1911).
22. Foth, G., *Chem.-Ztg.* **37**, 1221, 1297 (1913).
23. Demuth, R. v., *Z. angew. Chem.* **26**, 786 (1913).
24. Sherrard, E. C., and Kressman, F. W., *Ind. Eng. Chem.* **37**, 5 (1945).
25. Heuser, E., *Cellulosechemie* **1**, 41 (1920); Heuser, E., Zeh, L., and Aschan, B., *Z. angew. Chem.* **36**, 37 (1923).
26. Lüers, H., *Z. angew. Chem.* **43**, 455 (1930); **45**, 369 (1932).

27. Scholler, H., Dissertation, Munich, 1923.
28. Thiersch, F., *Z. physik. Chem.* **111**, 175 (1924).
29. Saeman, J. F., *Ind. Eng. Chem.* **37**, 43 (1945).
30. Scholler, H., *Zellstoff-Faser* **32**, 65 (1935); *Chem. Ztg.* **60**, 293 (1936); cf. also Faith, W. L., *Ind. Eng. Chem.* **37**, 9 (1945).
31. Ant-Wuorinen, O., *Svensk Papperstidn.* **45**, 149 (1942).
32. Cf. Gogarten, R., German Pat. 687,668 (1931).
33. Plow, R. H., Saeman, J. F., Turner, H. D., and Sherrard, E. C., *Ind. Eng. Chem.* **37**, 36 (1945).
34. Harris, E. E. and Beglinger, E., *Ind. Eng. Chem.* **38**, 890 (1946).
35. Harris, E. E., Hajny, G. J., Hannan, M., and Rogers, S. C., *Ind. Eng. Chem.* **38**, 896 (1946).
36. Heuser, E., *Cellulosechemie* **1**, 41 (1920).
37. Leonard, R. H., and Hajny, G. J., *Ind. Eng. Chem.* **37**, 390 (1945).
38. Grondal, B., and Berger, H. W., *Chem. & Met. Eng.* **52**, 6 (1945).
39. Fink, H., Lechner, R., and Heinisch, E., *Biochem. Z.* **278**, 23 (1935); **283**, 71 (1935); Fink, H., and Lechner, R., *Biochem. Z.*, **286**, 83 (1936).
40. Cf. Saeman, J. F., Locke, E. G., and Dickerman, G. K., Production of Wood Sugar in Germany and its Conversion to Yeast and Alcohol, Fiat Final Report No. 499 (1945), *Paper Trade J.* **123**, No. 12, 38 (1946); McGovern, J. N., and Dickerman, G. K., *ibid.* **124**, No. 2, 33 (1947).
41. Fingerling, G., and Honcamp, F., *Landw. Vers.-Sta.* **118**, 263 (1934); Scheunert, A., and Wagner, K. H., *Biochem. Z.* **303**, 329 (1940); Colonial Food Yeast Ltd., Food Yeast: A Venture in Practical Nutrition, 1944; Lewis, J. C., Stubbs, J. J., and Noble, W. M., *Arch. Biochem.* **4**, 389 (1944); Harris, E. E., Beglinger, E., Hajny, G. J., and Sherrard, E. C., *Ind. Eng. Chem.* **37**, 12 (1945).
42. Peterson, W. H., Snell, J. F., and Frazier, W. C., *Ind. Eng. Chem.* **37**, 30 (1945).
43. Harris, E. E., Beglinger, E., Hajny, G. J., and Sherrard, E. C., *Ind. Eng. Chem.* **37**, 12 (1945).
44. Hasche, R. L., *Ind. Eng. Chem.* **37**, 52 (1945).
45. Sherrard, E. C., and Beglinger, E., U.S. Pat. 1,932,255 (1933); 2,130,783 (1938); Sherrard, E. C., Beglinger, E., Hohf, F. P., and Bateman, E., U.S. Pat. 2,151,412 (1939).
46. Katzen, R., and Othmer, D. F., *Ind. Eng. Chem.* **34**, 314 (1942); Olson, E. T., Katzen, R., and Plow, R. H., U.S. Pat. 2,156,159 (1939); Olson, E. T., and Plow, R. H., U.S. Pat. 2,156,160 (1939).
47. Katzen, R., Sawyer, F. G., and Othmer, D. F., *Ind. Eng. Chem.* **37**, 1218 (1945).
48. Katzen, R., Aries, R. S., and Othmer, D. F., *Ind. Eng. Chem.* **37**, 442 (1945).
49. Braconnot, H., *Ann. chim. et phys.* [2] **12**, 172 (1819).
50. Flechsig, E., *Z. physiol. Chem.* **7**, 524 (1882).
51. Arnould, J. E., *Dinglers Polytech. J.* **134**, 219 (1852).
52. Classen, A., German Pat. 111,868 (1899).
53. Ekström, G., German Pat. 193,112, 207,354 (1906); cf. Hägglund, E., Die Hydrolyse der Zellulose und des Holzes, Sammlung chem. u. chem.-tech. Vorträge, vol. 22, Stuttgart, 1916, p. 443.
54. Unpublished results of E. Hägglund, W. Améen, T. Nilsson, D. Johansson, and T. Johnson.
55. Giordani, M., British Pat. 523,190 (1940).
56. Mitterbiller-Epp, K., German Pat. 678,543-44 (1939).

57. Waldhof Cellulose Works, and Hottenroth, V., German Pat. 310,149-50 (1917).
58. Budnikoff, P. P., *Z. angew. Chem.* [3] **36**, 326 (1923).
59. Béchamp, A., *Ann. chim. et phys.* **48**, 463 (1856); *Compt. rend.* **42**, 1213 (1856); cf. also Pelouze, M. F., *Compt. rend.* **48**, 327 (1859).
60. Dangevilliers, E. S., German Pat. 11,836 (1880).
61. Willstätter, R., German Pat. 273,800 (1913); Willstätter, R., and Zechmeister, L., *Ber.* **46**, 2401 (1913).
62. Cf. Häggglund, E., *Svensk Kem. Tid.* **35**, 2 (1923); *Papier-Fabr.* **25**, 52 (1927).
63. Ost, H., *Ber.* **46**, 2995 (1913).
64. Th. Goldschmidt Co., and Häggglund, E., German Pat. 391,969 (1917); Häggglund, E., U.S. Pat. 1,544,149 (1925).
65. Bergius, F., Färber, E., and Jellinek, O., *Ergebnisse angew. physik. Chem.* **1**, 199 (1931).
66. Bergius, F., *Ind. Eng. Chem.* **29**, 247 (1937); Häggglund, E., in *Handbok i kemisk teknologi*, vol. 4, Stockholm, 1949, p. 202.
67. Bergius, F., Koch, F., and Färber, E., U.S. Pat. 1,890,491 (1932); I. G. Farbenind. A.-G., Belgian Pat. 446,218 (1942).
68. Häggglund, E., Koch, F., and Löfman, N., German Pat. 382,463 (1920).
69. Wohl, A., *Cellulosechemie* **2**, 7 (1921).
70. Wohl, A., and Krull, H., *Cellulosechemie* **2**, 1 (1921).
71. German Pat. 304,399 (1916).
72. Terisse, H., and Levy, M., British Pat. 143,212, 154,170 (1920); French Pat. 511,924 (1920).
73. Darboven, J. W., German Pat. 569,549 (1933); cf. also Dreyfus, H., British Pat. 376,322-23 (1932) and Neu, E., French Pat. 825,254 (1938).
74. Cf. also Ormandy, W. R., *J. Soc. Chem. Ind. London* **45**, 267 T (1926).
75. Langhans, R., German Pat. 82,857 (1893).
76. Ostenberg, Z., U.S. Pat. 1,242,030 (1917); 1,315,393 (1919); 1,348,731 (1920).
77. Cross, C. F., and Bevan, E. J., *Chem. News* **63**, 66 (1891).
78. Fredenhagen, K., and Cadenbach, G., *Angew. Chem.* **46**, 113 (1933).
79. Fredenhagen, K., and Helferich, B., German Pat. 560,535 (1927).
80. Lüers, H., *Holz Roh- u. Werkstoff* **1**, 342 (1938).
81. Austrian Pat. 147,494 (1935); 151,241 (1936).
82. Schlubach, H. H., *Angew. Chem.* **45**, 245 (1932).
83. Harris, E. E., *Advances in Carbohydrate Chemistry*, Vol. 4, New York, 1949, p. 154.

CHAPTER V

THE PULPING OF WOOD WITH SOLUTIONS OF
SULFUROUS ACID AND SULFITES

I. History of the Sulfite Process

The wood pulp industry, like many other organic heavy-chemical industries, has its origin in discoveries made in the middle of the last century. In 1853 C. Watt and H. Burgess (1) in the United States succeeded in making pulp suitable for paper manufacture by heating wood with alkali under pressure, and 13 years later, in 1866, another American, B. C. Tilghman (2), found that a white pulp could be made by treating wood under pressure with solutions of sulfurous acid, or even better, of calcium bisulfite. Tilghman did not succeed in adapting his process to technical operation, however, primarily because the equipment which he used for the pulping was too complicated. It is impossible to say whether the next pioneers in this field, the Swede, C. D. Ekman, and the German, A. Mitscherlich, were familiar with Tilghman's work, but they succeeded in any case, independently of one another, in working out the sulfite-pulp process on a technical scale. It should be noted that Ekman produced sulfite pulp continuously from 1874 on, thus preceeding Mitscherlich by several years (3). The first sulfite-pulp plant was operated by Ekman at Bergvik in Sweden. The digesters were small, having a capacity of only 6 cubic meters, and were provided with double walls so that they could be heated with steam. They were pivoted, to make emptying of the charge easy when the cooking had been completed, and were lined with lead to resist the action of the acid. After the completion of the cook, the pulp was washed, beaten in a kind of Hollander beater, the water removed by centrifuging, and the wet pulp pressed to bring the water content down to 50%.

Great difficulties attended the operation of the first mill, and it was many years before it became possible to manufacture pulp at a profit. The improvements consisted in changes in the equipment and the mechanical details of the process, and the main interest centered from the very beginning on this phase of the operation. Particularly important was the introduction of large digesters by O. and R. Vogel at Hannover-Münden. This greatly increased the efficiency of the mills. The process first became profitable during the eighties, but the production was still comparatively insignificant, the great increase coming only at the turn of the century. To-

day the world production of sulfite pulp amounts to about 10 million tons. Simultaneously with the huge increase in production, there occurred a steady improvement in the equipment and organization of the mills, so that the costs of production decreased continually.

In the last few decades however, the question of the quality of the pulp has assumed more and more importance, and consequently the chemical processes involved in the production, particularly in the cooking have received more attention. It is now possible to conduct the cooking in such a way that the desired quality of pulp is achieved, and workers in the field have also gradually come to realize that proper carrying out of the cooking can result in considerably higher yields of pulp. These matters will be discussed below.

It is astonishing that the chemical processes involved in cooking sulfite pulp were not considered by either technical or scientific men until so recently. This neglect can be understood, however, in the light of the fact that sulfite pulp could be prepared even in ignorance of all theoretical considerations. It is true that spoiled cooks occurred quite often, but they were widely regarded as unavoidable.

Neither the inventor, Tilghman, nor his successors, Ekman and Mitscherlich, had any knowledge of the chemistry of the sulfite process. In the early days the experts on paper pulp had incorrect ideas about the course of the dissolution of the incrusting material by bisulfite solutions. The view was widespread that this was a reduction, since calcium sulfate had been found to arise during the cooking, and it was believed that the lime in the cooking acid was needed to neutralize the sulfuric acid, and thus prevent the destruction of the pulp.

It was only in the early nineties that orienting experiments were initiated by N. Pedersen (4) and by J. B. Lindsey and B. Tollens (5) which showed that the lignin reacted with the sulfite to form a soluble sulfonic acid. Part of the sulfurous acid proved to be firmly bound and the remainder, loosely. It was assumed that even the loosely-combined sulfite was attached exclusively to the lignin (6). Not until recently was it shown, however, that this view is incorrect, as will be discussed below (p. 429).

II. The Theory of the Sulfite Pulping Process and its Practical Consequences

A. THE CHEMISTRY OF SULFITE PULPING

1. Sulfonation and Delignification. The essential features of the theory of the sulfite-pulping process have been treated above (see p. 215). It was

shown that the dissolving of the lignin takes place in two stages: first a sulfonation of the lignin in the solid phase to produce solid lignosulfonic acid containing more or less sulfur, and secondly a solution of this acid to give water-soluble lignosulfonic acid. The speed of the last process is regu-

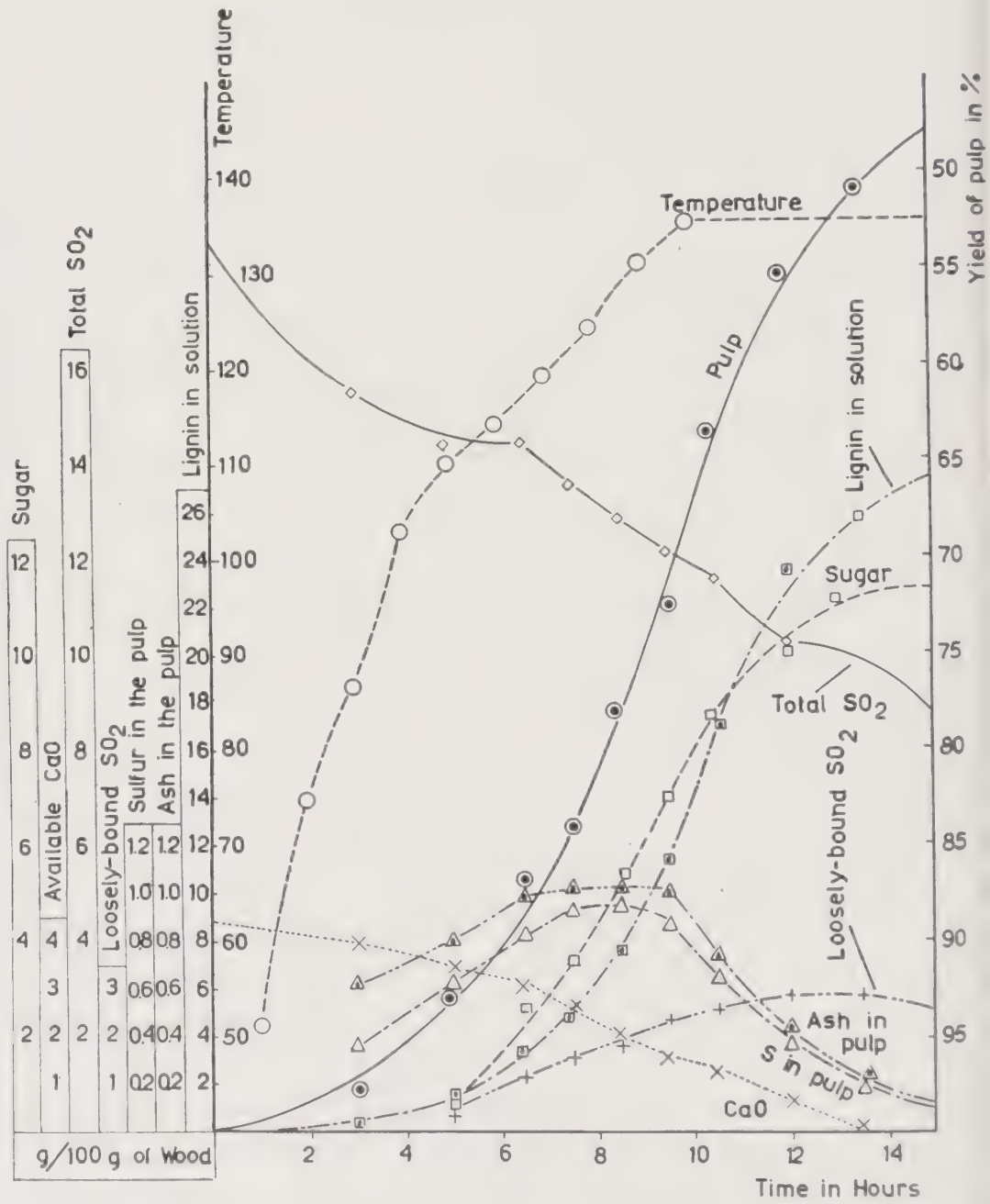


Fig. 69. Chemical composition of liquor and residue (pulp) at various stages of the normal sulfite cooking process.

Sulfonation, Delignification, and Other Changes Occurring During a Sulfite Cook

Cooking Time hrs.	Temperature °C	L i q u o r				P u l p						S 100 Lignin	Atomic Ratio S:C in Lignin			
		Color of Liquor	Avail-able CaO g./100 g. Wood	Total SO ₂ g./100 g. Wood	Loosely Bound SO ₂ g./100 g. Wood	Sugar (not Invert- ed) g./100 g. Wood	Yield g./100 g. Wood	L i g n i n			Ash Content			Sulfur Content		
								In Residue %	g./100 g. Wood	In Solu- tion g./100 g. Wood	%			g./100 g. Wood	%	g./100 g. Wood
3	87	Water-white	3.96	15.48	—	—	97.34	28.72	27.96	0.39	0.63	0.37	0.36	1.3	1 : 71	
5	110	Pale yellow	3.41	14.36	0.44	0.68	92.98	28.88	26.85	1.50	0.86	0.67	0.62	2.3	1 : 52	
6½	117	Pale yellow	3.12	14.40	1.20	2.56	87.08	28.69	24.99	3.36	1.13	0.94	0.82	3.3	1 : 43	
7½	121	Light yellow	2.56	13.52	1.56	3.56	84.12	27.77	23.36	4.99	1.21	1.11	0.93	4.0	1 : 37	
8½	127	Yellow	2.08	12.80	1.96	5.24	78.12	26.54	20.74	7.61	1.31	1.02	0.95	4.6	1 : 33	
9½	133	Yellow	1.56	12.12	2.36	6.96	72.48	23.33	16.91	11.44	1.41	1.02	0.88	5.2	1 : 33	
10½	135	Dark yellow	1.32	11.56	2.56	8.72	63.62	17.82	11.33	17.02	1.15	0.73	0.65	5.7	1 : 30	
12	135	Dark yellow	0.64	10.20	2.84	10.08	55.66	8.74	4.87	23.48	0.76	0.42	0.69	7.9	1 : 22	
13½	135	Brown	0.04	9.88	2.84	11.12	50.94	5.20	2.65	25.70	0.46	0.23	0.42	8.1	1 : 21	
15	135	Dark brown	—	8.80	2.56	11.32	47.40	2.32	1.40	27.25	0.31	0.15	0.11	—	—	

lated by the hydrogen ion concentration, and may be looked upon as an hydrolysis.

On the basis of this theory it is possible to understand the picture which one obtains by following the course of the cooking. This will be discussed in more detail with the aid of Fig. 69 and the table which goes with it.

The decrease in the total content of sulfurous acid is seen to be considerable, even at low temperatures, but a corresponding quantity of lignosulfonic acid does not go into solution. Apparently the wood binds appreciable quantities of sulfurous acid from the very beginning; this uptake of SO_2 is probably at first a pure adsorption, but when the temperature has reached a certain point chemical combination occurs, and from this moment on, the calcium ion content of the solution decreases. At this stage of the cooking the calcium salt of the solid lignosulfonic acid is formed.

At first, only small amounts of carbohydrates go into solution; the weight of the residue therefore decreases only slightly. In the course of the cooking further quantities of bisulfite and calcium ions are removed from the cooking liquor and bound to the lignin, as may be seen from the sulfur and ash content of the residue.

The temperature has meanwhile risen, and the hydrolyzing action of the cooking liquor becomes more manifest; the point is soon reached at which the binding of SO_2 to the lignin and the dissolving out of the lignosulfonic acid from the residue proceed with equal speed. With further increase in temperature, the hydrolysis predominates, as is indicated by the rapidly decreasing sulfur and ash content of the residue. Large quantities of lignin go into solution; the formation of sugar proceeds concurrently. (Cf. Table, p. 417.)

At this point we would like to examine the sulfonation process more closely. It has already been emphasized that sulfonation of lignin takes place with appreciable velocity even at temperatures of 60-70° C (7). This is true both in acid and in weakly alkaline media, but the reaction is more rapid in acid.

The sulfur content of the finished sulfite pulp amounts to one sulfur atom for each 20 carbon atoms of the lignin remaining in the pulp. Under special conditions it can be shown that the uptake of sulfur to form solid lignosulfonic acid occurs stepwise. Thus, when extracted sawdust from spruce was treated at 135° C with a 15% sodium sulfite solution of pH 6, the liquor being changed after every 20 hours, a lignosulfonic acid containing 1 S for each 3.5 methoxyls (corresponding to 1 S for each 35-40 C) was formed rather rapidly, while further sulfonation proceeded very slowly. This is illustrated by the following table (8).

Cooking Time at 135°C	Residue %	Sulfur %	CH ₃ O %	S/Na
5	91.2	1.03	4.51	1:1.05
10	89.6	1.08	4.45	1:1.11
20	83.6	1.19	4.42	1:1.13
30	80.0	1.27	3.75	1:1.11
50	77.9	1.19	3.48	
60	74.8	1.09	3.43	

If the wood is pulped with sodium bisulfite, the sulfur is taken up considerably more quickly, as may be seen from the following figures (9). It is to be noted that the sulfonation proceeds much further here, and apparently finally reaches a limiting value of 1 S to 20 C.

20 g. of Spruce Wood Pulped with 100 cc. of 6% NaHSO₃ at 120°C

Cooking Time in hrs.	Residue %	Sulfur %	Lignin in Residue %	$\frac{S \times 100}{\text{Lignin}}$
2	94.1	0.70	—	—
4	92.6	0.82	23.4	3.5
6	91.3	0.91	20.3	4.1
8	89.9	1.12	19.2	5.9
10	88.4	1.25	17.8	6.1
12	86.9	1.37	16.6	8.3
14	84.0	1.31	15.2	8.6

When the acidity of the cooking liquor is still higher, as it ordinarily is in sulfite pulping, the velocity of sulfonation is still greater, as was proved in the same studies (9). It can be calculated that three hours at 120°C suffice to bring the sulfur content of the lignin to 5.8%. The further uptake of sulfur also follows quickly, but the speed of dissolving increases so rapidly at the same time that only small quantities of solid liginosulfonic acid with a high content of sulfur can be detected in the resulting pulp.

The above-mentioned solid liginosulfonic acid with 1 S to about 3.5 methoxyls appears very quickly during pulping with acid solutions, too. This is not a statistical average, for Hägglund has found that a fractional dissolution like that described above (p. 197) gave a series of values for the CH₃O: S ratio lying between 3.5 and 3.9 for 80% of the liginosulfonic acid, and that even in the residue, the ratio was still 3.6.

The experiments further showed that the concentration of the bisulfite ions is important in the sulfonation. Pulping with cooking acids rich in bisulfite gave residues or pulps which contained comparatively much highly sulfonated lignin.

This finding appears to be of great significance for the attempt to attain increased yields of pulp. Experiments (10) on this point have led to the following results.

Spruce chips were pulped with calcium bisulfite cooking liquors which contained varying amounts of CaO, but the same amounts of SO₂, and the following results were obtained:

CaO Content g./100 cc.	Yield of Pulp in g./100 g. Wood at Roe number ¹ of		
	10	5	3
0.6	55.0	52.2	50.7
1.0	57.8	54.0	51.9
1.4	58.6	54.7	52.7

It will be seen from the table that the increase in yield on going from a CaO content of 0.6% to 1.0% is greater than that on going from 1.0% to 1.4%.

It is possible to increase the yield considerably more by increasing the SO₂ content at the same time as the CaO concentration (12).²

Such a procedure raises the pressure in the digester above the usually allowable level. However, precisely because of the advantages which attend the cooking with "strong" sulfite liquors, digesters have recently been introduced and operated which permit pulping at pressures of 10 atm. or more.

Hand in hand with the increase in the yield goes an improvement in the strength of the pulp.

It is quite clear that the various pulps must differ considerably in the compositions of their carbohydrate components, for as the yield increases, more of the wood polyoses must remain in the pulp. This is easily understood on the basis of the previously mentioned findings, that the solution of the lignin and of the wood polyoses are both hydrolytic processes. The yield of pulp at a given lignin content depends, therefore, on the speed of hydrolysis of the solid lignosulfonic acid compared with that of the hydrolysis of the easily hydrolyzable wood polyoses.

The slightly sulfonated lignosulfonic acid with one sulfur to about 10 carbon atoms is, as was mentioned before, more difficult to dissolve out than the completely sulfonated acid with one sulfur to 20 carbons. This is clearly demonstrated in the following figures of E. Hägglund, T. Johnson, and H. Busch on the extraction of lignosulfonic acid with hot water (80°C) after cation exchange (8).

¹ The Roe number is a value for the chlorine consumption of the pulp, i.e., a measure of its lignin content (11).

² This has been completely confirmed in large scale operation. Cf. M. F. Martynov (13).

	A Sulfonated Wood 5 hrs. at 135° C pH ~ 6	B Sulfonated Wood 21 hrs. at 135° C pH ~ 3.8 + 2 hrs. at 135° C pH 2.5
Yield in %.....	91.2	67.0
Sulfur content in %.....	1.03	1.085
Lignin content, sulfur-free, in %.....	26	14.9
Ratio of S to lignin, %.....	4	7.3
Heating time at 80° C, hrs.....	83	13
Lignosulfonic acid dissolved out, %.....	67	67
Lignin dissolved out, g.	15.8	6.7
Lignin dissolved out per hour, g.	0.19	0.52
Ratio of S:CH ₃ O in the lignosulfonic acid washed out	1 : 3.75	1 : 2.09
Sulfur in residue %.....	0.34	0.36

It is not yet completely clear why the dissolution of the lignin is accelerated by further sulfonation (cf. p. 216). In the example given above the sulfur content of the wood was practically the same in the two cases, so that the hydrogen ion concentrations of the solid phases should be about the same if the hydrogen ions are distributed throughout the entire fiber mass; if the hydrogen ion concentration is referred to the lignin portion, it is of course twice as great in case B as in case A.

It also has to be considered that the further sulfonation of a low-sulfonated lignin involves the splitting of hydrolyzable linkages. As a result, the amount of residual linkages to be hydrolyzed during the hot water extraction will be relatively low in the higher sulfonated product. The extraction of this product will, therefore, be easier than that of the low-sulfonated one.

The results of O. Maass and his co-workers (14) are also explained by these investigations. Maass found that the delignification is dependent not alone of the hydrogen ion concentration, but also on the concentration of the bisulfite ions if one considers the total effect of the pulping with bisulfite. This is quite clear, indeed, for as we have previously shown (10), an increase in the bisulfite ion concentration accelerates the sulfonation. The sulfonation is also dependent on the prevailing acidity. On the other hand, as is well known (15), the acidity of the solution affects the actual hydrogen ion concentration in the solid phase, and this again determines the rate at which the solid lignosulfonic acid is dissolved out.

Maass and his collaborators, on the basis of their kinetic measurements, came to the conclusion, that the delignification is pseudomonomolecular, its rate being approximately proportional to the amount of undissolved lignin. G. Goldfinger (16), calculating the order of reaction for the delignification process during sulfite cooking, states that the reaction is complex and that the results achieved do not allow any interpretation concerning the mechanism of the reaction.

At a constant concentration of metal ions, such as exists during sulfite pulping, the effective concentration of hydrogen ions in the solid phase is determined by the acidity of the cooking liquor. Hence it is interesting to determine this acidity.

A number of investigators have looked into this problem. R. Escourrou and P. Carpentier (17) determined the hydrogen ion concentration at room temperature by electrometric or colorimetric methods, and found that the

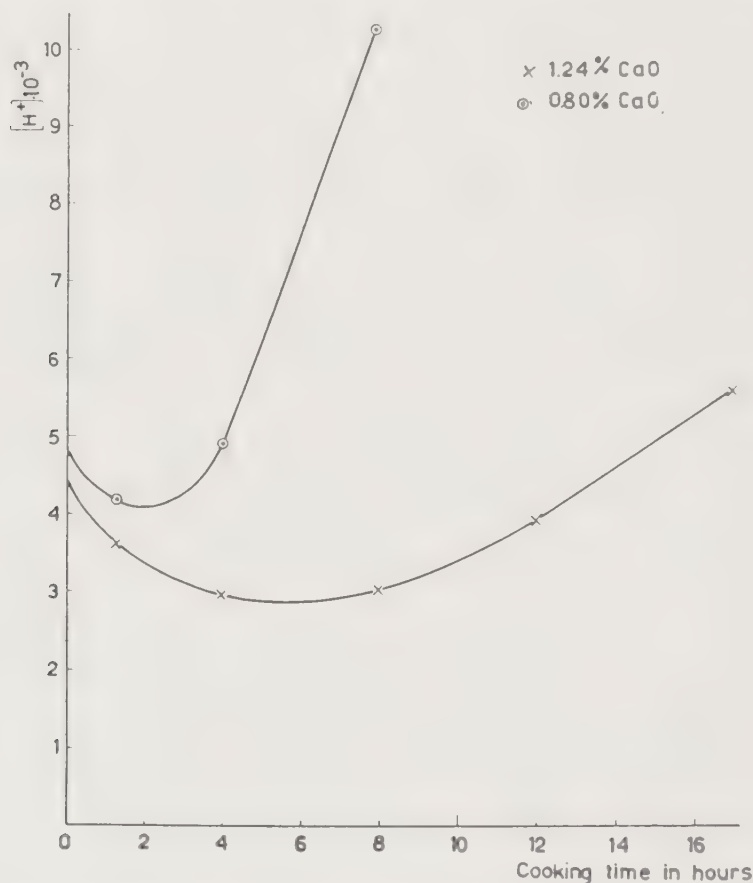


Fig. 70. Hydrogen ion concentrations of two different cooking liquors during the cooking process.

pH rose from 1.7 to 2.5-3.0 during the impregnating period. As the cooking proceeded, the pH fell to 1.8-2.0. These findings constituted at least qualitative confirmation of earlier results (18), in which the pH had been determined indirectly by inversion measurements at low temperature.

Other procedures are necessary to determine the acidity of the sulfite liquor during the cooking. E. Häggglund and A. Johansson (19) determined the hydrogen ion concentration by measuring the rate of the conversion

of soluble starch to sugar at the cooking temperature. Two different pulping liquors were investigated:

Liquor I: 5 g. SO_2 and 1.24 g. CaO per 100 cc.

Liquor II: 5 g. SO_2 and 0.80 g. CaO per 100 cc.

The results are given graphically in Fig. 70.

It is seen that a decrease in the hydrogen ion concentration of the liquor occurs first, and that subsequently the acidity rises more or less rapidly, depending on the lime content of the liquor. It should be noted that the acidity is considerably less than that measured at ordinary temperature. That is, the hydrogen ion concentration decreases very rapidly with rising temperature, as was also found by W. B. Campbell and O. Maass (20), who made extensive studies of the equilibria existing in solutions of sulfurous acid. They established the fact, for example, that the hydrogen ion concentration of a liquor containing 5.12% of total SO_2 and 1.28% bound SO_2 was 0.002 M at 100°C.

According to these authors, one would have to assume that such a small hydrogen ion concentration would have no hydrolytic effect. Then the acidify of the cooking liquor would have no influence on the sulfite pulping process. This is certainly not correct, for both soluble starch and the easily hydrolyzable wood polyoses are readily hydrolyzed at this hydrogen ion concentration.

The hydrogen ion concentration certainly does not decrease to such an extent that at one point in the pulping there occurs an "alkaline hydrolysis" as was assumed by W. H. Birchard (21).

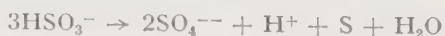
The acidity of the cooking liquor corresponds, as has been mentioned frequently, to a definite acidity of the solid lignosulfonic acid. If this acidity becomes too great, a condensation occurs at sufficiently high temperatures, giving rise to a darkening of the pulp. This is known as "burnt cook" (22). The risk of burnt cook is great when the lime content of the liquor is too small and the temperature too high (23). When wood is pulped with sulfurous acid alone, care must therefore be exercised that the temperature does not become too high.

The partially sulfonated lignin is particularly sensitive. From recent experiments performed at the author's institute by I. Hedlund (24), it has become evident, that the condensation of such low-sulfonated lignin depends on the actual acidity in the solid phase. Spruce wood was pre-sulfonated by two or five hours heating at 120°C with a sodium bisulfite cooking acid and thereafter the heating was continued for different times with either sodium phosphate buffer solution of pH 2 or a phosphoric acid solution of the same pH. After this treatment the samples were pulped again with sodium bisulfite cooking acid, the total time of sulfite pulping

being equal in all experiments. Those low-sulfonated samples which had been treated with the sodium phosphate buffer, were easily delignified by the final sulfite cooking, whilst the treatment with free phosphoric acid resulted in a more or less complete condensation ("burnt cook"). Thus it is obvious that the solid, low-sulfonated lignin in the state of the free acid, effectively catalyzes its self-condensation. Metal ions in the surrounding solution, favoring the formation of solid lignosulfonic salts by cation exchange, are able to neutralize this catalytic effect to a high degree.

The sulfite cooking acid appears to attack primarily the lignin which is deposited in the compound middle lamella. This information has been obtained by P. W. Lange (24 a) in his studies concerning the ultraviolet absorption of lignin in the wood fiber. During sulfite digestion the decrease in ultraviolet absorbing material, i.e., in lignin, occurs faster in the middle lamella than in the secondary wall. On the basis of cooking experiments with ammonium bisulfite solution, O. Bryde (24 b) concluded that the process can be subdivided into three rather characteristic stages. He assumed that the first stage consists of a breaking down of the middle lamella and a splitting of a presumed linkage between lignin and carbohydrates. The second stage is characterized by the dissolution of liberated lignin, and the third stage involves an attack on the cellulose.

2. Stability of Cooking Acid. Bisulfite solutions are unstable, particularly at high temperatures, and decomposition proceeds more or less rapidly. This reaction has been studied by several investigators, most thoroughly by F. Foerster (25) and his co-workers. A particularly important intermediate in the decomposition is the thiosulfate ion, which catalytically accelerates the decomposition. The overall decomposition corresponds to the equation



Hydrogen ions play a great part in the decomposition. Foerster states that they can retard the reaction by decomposing the thiosulfate, but it is obvious that they can also accelerate it, by removing the thiosulfate and converting it to pentathionate,



The pentathionate can be further decomposed, the final product being sulfate ions.

As E. Hägglund and his co-workers have found (26), this reaction is particularly important in sulfite pulping liquors. It turned out that the stability of the cooking liquor during the pulping process increased with the content of base; this is due to a diminished formation of sulfuric acid. On

the other hand, however, the thiosulfate formation increases with the higher base content, and the $S_2O_3^{--}$ ion concentration becomes rather high. When liquors high in base are used, a higher thiosulfate concentration is evidently compatible with stability of the liquor.

The fact that quite small amounts of selenium in the cooking liquor sharply decrease its stability is of extremely great importance in technical operations. P. Klason (27) was the first to call attention to this danger, and reported that 0.5 mg. of selenium in a liter of cooking liquor could cause such great decomposition that in the normal cooking time and with a maximum temperature of 135°C all of the sulfite would precipitate out as calcium sulfate. "Burnt cook" would of course be unavoidable under these circumstances. The presence of selenium gives rise to $SSeO_3^-$ ions which have a much stronger effect on the decomposition than does thiosulfate.

It turned out, however, that by cooking with *pure* cooking acid with selenium additions, it was possible to prepare pulp of high quality even with a selenium content of 0.75 mg. per liter. A distinct impairment of the quality of the pulp was observed only when the selenium concentration reached 1-2 mg. per liter. The stability of the cooking liquor is dependent not only on the selenium content, but also on other substances, such as terpenes, which enter in variable quantities into the composition of technical cooking liquors. In the presence of terpenes, lower concentrations of selenium are injurious (26).

These facts explain the earlier reports of the injurious effects of selenium in technical operations, where as little as 0.12 mg. per liter can sometimes cause failure of the cook (28).

Thiosulfate ions, which catalyze the decomposition of bisulfite cooking liquors, can also arise during the cook as a product of oxido-reduction between bisulfite ions and the sugars of the liquor (see p. 431). According to L. Stockman (28a), the reaction between bisulfite ions and formic acid also results in the formation of thiosulfate ions. The occurrence of formic acid in sulfite liquor has been shown previously (138). In an analogous manner, reactions between terpenes and bisulfite, leading to the formation of thiosulfate (see p. 458), also contribute to a diminution of the stability of the cooking acid.

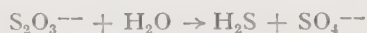
As the occurrence of these thiosulfate-forming reactions during the cook seems to be well established, it is a striking fact that decomposition of the cooking acid under normal conditions remains relatively limited. As O. Samuelson and A. Westlin (29) have pointed out, one might expect, on the basis of the available knowledge concerning the decomposition of sulfurous acid or bisulfite, that the formation of thiosulfate during the cook would result in a rapid total disproportionation of the bisulfite, giving

sulfate and thiosulfate, polythionates and sulfur. Analytical determinations, however, showed that the amounts of thiosulfate and polythionates present in various sulfite waste liquors, are very low.

Polythionates and Thiosulfate in Sulfite Waste Liquors

Sulfite Waste Liquor from	Polythionate ($S_4O_6^{--}$) g./l.	Thiosulfate ($S_2O_3^{--}$) g./l.
Rayon pulp, spruce.....	0.08	0.25
" " " ".....	0.05	0.14
Paper pulp, spruce.....	0.10	0.12
Paper pulp, aspen.....	0.08	0.11

Elementary sulfur is not precipitated in normal sulfite cooking, but it can be found in burnt cooks. Samuelson and Westlin assume that thiosulfate, which is formed as a product of the spontaneous decomposition of the sulfurous acid and the reactions of sulfurous acid with sugars and terpenes, is destroyed during the cook. As a possible mechanism they suggest the well-known decomposition of thiosulfate to hydrogen sulfide and sulfate:



The presence of small amounts of H_2S in the gas space of the sulfite digester could be shown. B. Groth (30) had previously proved its presence in sulfite waste liquor. The bulk of the H_2S formed from thiosulfate might, according to a suggestion of Samuelson and Westlin, react with lignin or with constituents of the cooking liquor (cf. p. 225).

The consumption of sulfur in sulfite pulping can vary over a relatively wide range. Sulfur is consumed by (1) the sulfonation of lignin, (2) greater or lesser degree of decomposition of sulfite to sulfur, sulfate, and thiosulfate, and (3) the binding of SO_2 to sugars and other aldehydes. The total sulfur consumption varies between 70 and 100 kg. per ton of pulp.

3. Sulfate Formation. The cooking liquor itself always contains a certain amount of SO_4^{--} ions, even when the burner gases have been carefully freed of sulfur trioxide. The reason for this is that sulfurous acid is oxidized in water solution. E. Hägglund and L. Waenerlund (31) found that this oxidation can be practically stopped by adding relatively small quantities of sulfite waste liquor to the water in which the sulfur dioxide is to be absorbed. This is illustrated by the following figures:

Cooking acids were prepared by passing SO_2 into pure water or into water containing 5 or 25 % of waste liquor. The SO_2 content was 5.5% and the CaO , 1%. These acids were shaken with oxygen for 20 minutes at 17°C.

Volume % of Sulfite Waste Liquor Added	0	5	25
	mg. SO_4^{--} per l.		
Original SO_4^{--} content	265	284	708
SO_4^{--} content after oxygenation	3,170	812	844
Increase in SO_4^{--} content	2,905	528	136

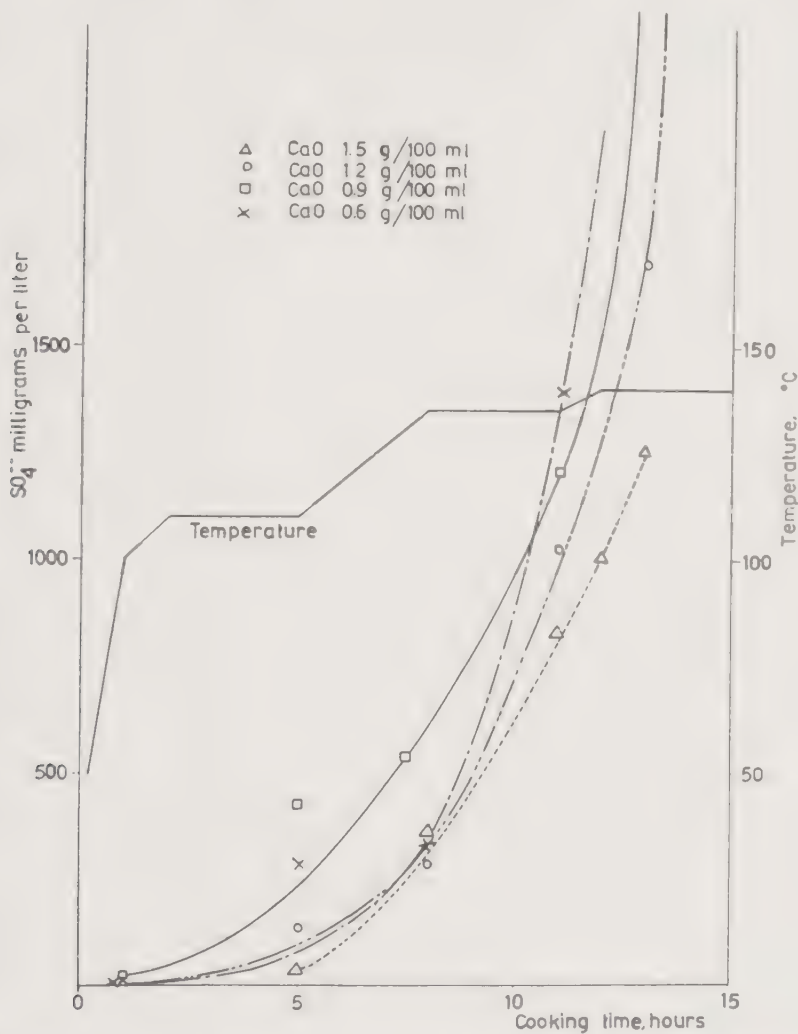


Fig. 71. Sulfate formation during calcium bisulfite cooks of spruce wood. Ratio cooking acid: wood — 4.3 : 1. Total sulfurous acid 5.5 g. in 100 ml.

Further quantities of sulfate ions are formed during the cooking process, as has been shown by Hägglund and co-workers (26). Since new, reliable methods for the quantitative determinations of sulfate ions in sulfite waste liquors have been developed by L. G. Sillén and O. Samuelson and their co-workers (32, 33), the formation of sulfate during the sulfite cook as well as during displacement, neutralization, fermentation and evaporation of the spent liquor has been studied in detail (34). O. Samuelson has

shown that the initial sulfate content of the cooking liquor decreases during the cook, before the maximum temperature is reached. This can be explained by a deposition of calcium sulfate on the pulp, due to its diminished solubility at elevated temperatures. In fact, it had been observed previously that fresh pulp coming from the digester, occasionally contains crystals of anhydrous calcium sulfate, which are sometimes removed only by the screens.

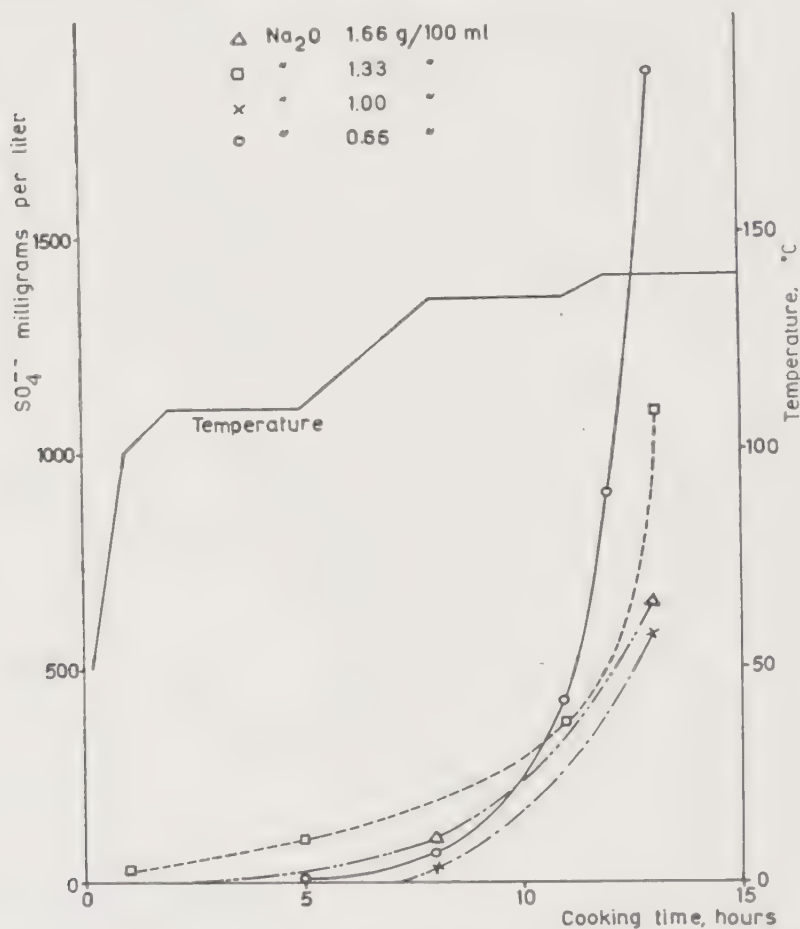


Fig. 72. Sulfate formation during sodium bisulfite cooks of spruce wood. Conditions are the same as in Fig. 71.

The formation of sulfate ions during the cook has been clearly demonstrated in laboratory experiments performed by E. Hägglund, A. Julander, N. Mannbro, and L. Waenerlund [cf. L. G. Sillén (34)]. In these experiments the cooks were allowed to cool to room temperature before the samples were taken. During the cooling period the CaSO_4 deposited on the pulp was dissolved again, the SO_4^{--} determinations thus giving the total amount of the sulfate present. Fig. 71 and 72 show the formation

of sulfate ions in calcium and sodium bisulfite cooks at different base contents. The cooks were performed in glass tubes. In order to avoid air oxidation of SO_2 , the chips were steamed for 10 minutes, the tubes evacuated and the cooking acid sucked in.

A redissolving of calcium sulfate precipitated on the pulp also occurs during the displacement of the waste liquor in technical operation. The final concentration of SO_4^{--} ions in unneutralized sulfite waste liquors varies between 600 and 1,500 milligrams per liter.

Data concerning the sulfate content of waste liquors are of special interest in connection with the attempts (made especially in Sweden) to find a satisfactory method of evaporating and burning sulfite waste liquors (35). One of the greatest difficulties is the scale formation during evaporation caused by calcium sulfate. It is, therefore, of great importance to keep the sulfate content of the waste liquor at the lowest possible level.

4. Loosely Bound Sulfur Dioxide. From technical sulfite waste liquor the gas has been relieved at the end of the cooking process and therefore such liquor contains very little sulfurous acid which can be titrated directly with iodine solution. On the other hand, the waste liquor always contains appreciable amounts of "loosely bound" sulfurous acid. It may be liberated by making the liquor alkaline for some minutes and can then be titrated after the liquor has been acidified with mineral acid. It can also be removed by distillation, provided that the pH of the liquor is low enough. This "loosely bound" SO_2 amounts to 4-8 grams per liter in waste liquors from strong pulps and to 2-4 grams per liter in waste liquors from rayon pulps and has the character of carbonyl bisulfite addition products [W. Kerp and P. Wöhler (36), E. Adler (37)]. The chemical nature of the carbonyl compounds responsible for the binding of bisulfite in the waste liquors, has recently been elucidated to a great extent. It has been shown independently by E. Adler (38) and J. Sundman (39), that—in contrast to the old assumption of Kerp (36)—the sugars present in the waste liquor are of no importance in this connection. Sugar bisulfite addition compounds are in solution highly dissociated into their components and they are therefore practically completely split when the excess of sulfurous acid is removed during the last stages of a cook. O. Samuelsson (40) found that waste liquors contain volatile aldehydes forming relatively stable bisulfite compounds, and E. Adler (38) has identified these substances as formaldehyde, methylglyoxal, and furfural. The aldehyde content of two different waste liquors is shown in the following table:

Free and Loosely Bound SO₂ and Volatile Aldehydes in Sulfite Waste Liquor (38)

Sulfite Waste Liquor from	Millimoles per Liter Waste Liquor				
	Free SO ₂	Loosely Bound SO ₂	Formal- dehyde	Methyl- glyoxal	Furfural
Strong pulp.....	5	81	6	9	6
Rayon pulp.....	4	31	18	7	6

The bisulfite addition products of formaldehyde and methylglyoxal are practically undissociated in aqueous solution, i.e., the equilibrium



lies very far to the left side. Hence, these two aldehydes occur in the waste liquor in the form of their bisulfite compounds. The figures given in the above table mean, therefore, that in a rayon pulp liquor the main part of the loosely bound SO₂ is attached to the volatile aldehydes. On the other hand, in liquors from strong pulp, the volatile aldehydes will only account for a smaller part of the total loosely bound SO₂. In such liquors, another part of the loosely combined SO₂ is bound by carbonyl groups and especially by coniferaldehyde groups occurring in lignosulfonic acids (38, cf. also p. 189). The bearing of these results on the neutralization and fermentation of sulfite waste liquors will be discussed below (see p. 459).

5. Formation and Destruction of Sugar During the Sulfite Cook. The formation of reducing sugar naturally depends on the acidity and temperature of the cooking liquor. The following results were obtained, for example, when wood was pulped with sodium bisulfite solutions (41):

Pulping with 12% Sodium Bisulfite Solution at 130°C.
Ratio of Liquid to Wood 5:1

Cooking Time in hrs.	Color of Liquor	Yield of Pulp g./100 g. Wood	Lignin Content of Pulp %	Reducing Sugar in Cooking Liquor g./100 g. Wood	
				Not Inverted	Inverted
8	Light yellow	78	15.6	1.24	5.79
10	" "	76	12.5	1.61	6.43
12	" "	72	10.4	1.72	6.75
14	" "	70	—	1.82	7.39
16	" "	67	8.5	2.14	7.59

The ratio between the reducing powers of inverted and not inverted cooking liquor was about 4:1. Later investigations by E. Hägglund and R. Larson (42) have shown that when spruce sawdust was hydrolyzed at 130°C with acetic acid-acetate buffers of pH 4, a third of the dissolved carbohydrate consisted of simple sugars, and the remainder of a mixture of polysaccharides.

It also turned out that when the wood polyoses were dissolved out at the same time as the lignin, as is the case during sulfite cooking, both the extraction and the saccharification were made very much easier. It would appear that in the intact wood a certain part of the wood polyoses is in some manner protected against attack by acid.

Ordinary sulfite waste liquors do not contain appreciable amounts of polysaccharides. It is true that B. J. Lindsey and B. Tollens (13) found an increase in the alcohol yield from 0.588 to 0.675 volume percent when the waste liquor was heated with 4% sulfuric acid before fermentation, but there could be other explanations for this. Only monomeric sugars are present in general.

The assumption of the presence of polysaccharides would in any case not explain the great variations which occur in the sugar content of the spent liquors. A cooking acid containing 1.4 g. CaO and 4.74 g. SO₂ per 100 cc. gave 9.61 g. of sugar per 100 g. of wood after 19 hours cooking to a yield of 46% of pulp. A cooking liquor with 0.62 g. CaO and 4.83 g. SO₂ gave 20.3% of sugar in 15 hours when the cooking was carried to the same yield of pulp, the temperature being raised along the same curve (14). Since the difference in acidity of the two liquors cannot be very great, one must conclude that the acidity of the cooking liquor is not the only factor controlling the yield of reducing substances.

It was assumed for a long time that the sugar is decomposed during sulfite pulping in the same manner in which sugars have been observed to be degraded by heating under pressure with dilute mineral acids. However, this explanation is unsatisfactory when one considers the very slight acidity of the solution during the normal sulfite cooking. It has also been found that a reversion of the sugar to non-reducing compounds does not occur; this is quite understandable, since the sugar concentration is too low (45).

The investigations of E. Hägglund and his co-workers (16) into the decomposition of bisulfite solutions in the presence of various sugars have contributed to the explanation of this matter. The surprising result was obtained that bisulfite ions oxidize sugars with the formation of thio-sulfate ions and aldonic acids:



According to this equation the speed of sugar destruction must increase with increasing concentration of bisulfite ions and of sugar; this was confirmed.

Further investigations (17) have shown that this reaction probably proceeds in three stages. The bisulfite addition compound of the sugar is

formed first; the addition compound and the bisulfite ions form an oxidation-reduction system in which the addition compound acts as a hydrogen donor and the bisulfite ions as acceptor. Presumably an unstable keto-sulfonic acid is formed, and then splits hydrolytically to give the aldonic acid:

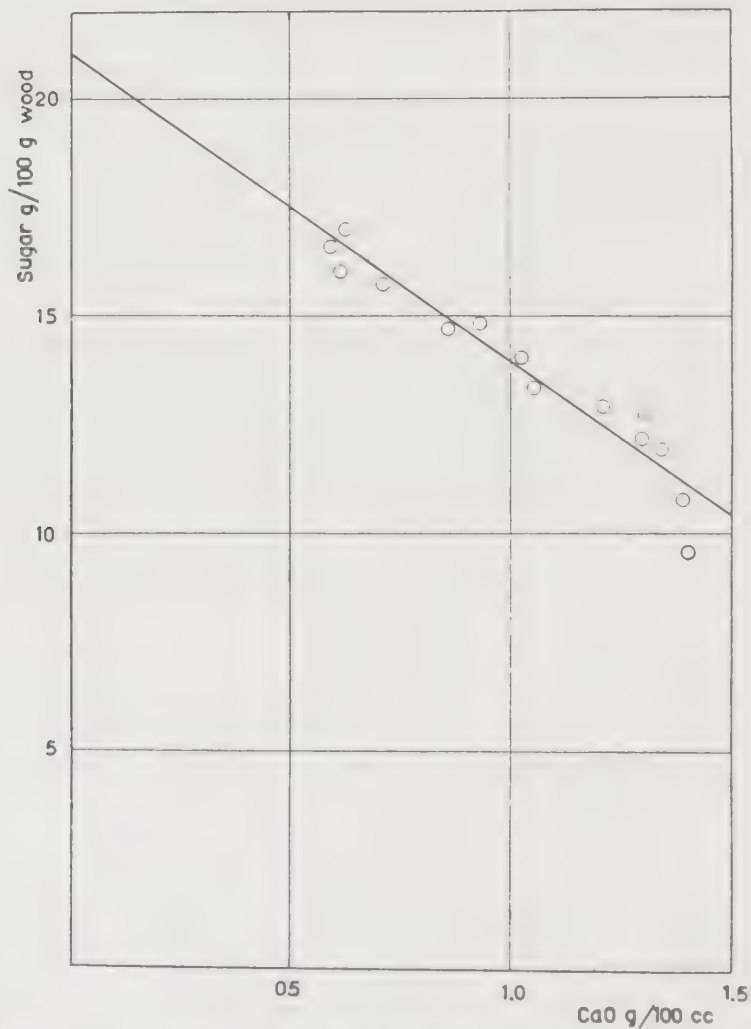
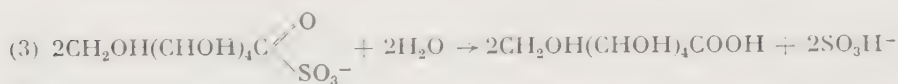
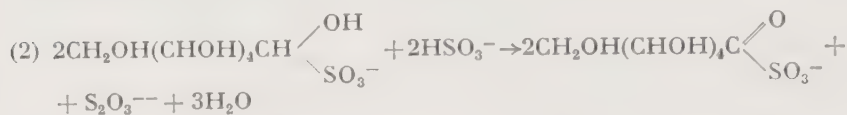


Fig. 73. The relationship between the yield of sugar from a sulfite cook and the lime content of the cooking liquor.

The relationship between the yield of sugar and the lime content of the cooking liquor is shown in Fig. 73. It will be seen that the curve is linear. The relationship between the amounts of wood and of acid was 1:5 in this case.

Not only the bisulfite ion content of the liquor, but also the temperature curve of the cooking is important in determining the yield of sugar. The investigations of E. Hägglund and H. Nihlén (48) revealed that the manner in which the temperature is raised can cause considerable differences in the yields of sugar. The explanation of this is that the rates of the formation of sugar and of its oxidation, and the temperature coefficients of these reactions are different.

Formic acid, which may be looked upon as the simplest hydroxyaldehyde, appears to react with bisulfite in the same manner as aldo-sugars. The formic acid is oxidized to carbon dioxide and water, while the bisulfite is reduced to thiosulfate (28a).

It has already been mentioned that selenium and terpenes, which may occur in the cooking liquor, diminish the stability of the bisulfite. The considerations introduced just now indicate that the presence of sugars as well as of formic acid has the same effect because of the formation of thiosulfate ions, which catalyze the decomposition of sulfurous acid (cf. p. 424). It is quite common to prepare cooking liquor by drawing off a quantity of the liquor from a digester at high temperature, and mixing it with "fresh liquor" (i.e., pure sulfite cooking acid). When this was done, it was often noticed that the whiteness and quality of the fibers were impaired, but the cause was not known (49). Experimental tests revealed that the use of "mixed liquor" consisting of one third sulfite waste liquor resulted in pulp of lower quality, and it was possible to link this effect to the more rapid decomposition of the sulfite caused by the sugar content of the waste liquor (50). Recently, it has been shown by E. Hägglund, L. Stockman, and P. Löfström (50a) that it is possible to use "mixed liquor" without impairing the pulp, if the cooking temperature is kept below 115°C. In this way, waste liquors of high dry substance content are obtained. The procedure appears to be feasible from the point of view of heat economy, especially when the waste liquor, after fermentation, is to be evaporated and burned.

The oxidation of aldoses to aldonic acids, described above, is not the only reaction which decreases the yield of sugar from the sulfite pulping process. Recent studies (51) have shown, that the heating of holocellulose with sulfite cooking liquors of usual composition causes the formation not only of aldonic acids but also of sulfonic acids, which differ from sugar-bisulfite addition compounds in that the sulfonic acid groups can not be

split off either with cold dilute alkali or with hot, dilute mineral acids. They are, therefore, true sulfonic acids, derived from the sugars. It has also been shown to be probable that they occur in the sulfite waste liquor from spruce pulping (52). Sugar derivatives with stable sulfonic acid groups and with aldehyde and carboxylic acid groups were first obtained by E. Hägglund, T. Johnson, and H. Urban (47) by heating glucose in neutral sodium sulfite solution. Recent investigations made in Hägglund's laboratory by E. Adler (53) have shown that two different sulfocarboxylic acids, a reducing as well as a non-reducing one, are thus formed. Their composition is $C_4H_7O_2(CHO)(COOH)(SO_3H)$ and $C_5H_{10}O_3(COOH)(SO_3H)$, respectively.

The relationship between these glucose derivatives, obtained at pH 6-7, and the sulfonic acids arising from holocellulose or wood during technical cooking procedures remains to be explained.

As the oxidation of aldoses to aldonic acids is favored by a high concentration of bisulfite ions (see above, p. 431), sugar destruction is higher in base-rich (strong pulp) than in rayon pulp cookings. Thus, the loss of sugars in pulpings of the two types has been estimated at 54 and 43% respectively (54). When holocellulose was cooked with acid calcium bisulfite liquor, it was found, that approximately one third of the total acids formed consisted of sulfonic acids (53).

6. Available Sulfite and Color Change in Cooking Liquor. It has already been mentioned that the acidity of the cooking liquor during the cooking is not constant, but changes in a characteristic way (cf. p. 422). Since lignosulfonic acid and sulfuric acid are continually formed, and since both are strong acids, the buffer capacity of the bisulfite solution decreases, and the content of available lime in the liquor diminished. The decrease in buffering action is accompanied by a change in color of the liquor from light yellow to brown, and finally to dark brown. This change in color can be used as an indication of the disappearance of "available sulfite."

This method is often the only one used to determine when the cooking should be stopped. The color of the liquor is compared with colored glass standards, or with liquids of various colors.

It is very important to heed this change in color if pulp of high quality is desired. The cooking must not be continued much beyond this point if strong pulp is to be made, for both the color and the strength of the pulp will be impaired (55).

According to E. Hägglund, T. Johnson, and L. H. Trygg (56) the change in color is to be explained as follows. So long as sufficient quantities of bisulfite ions are present in the liquor, it remains pale yellow, and the

pulp is pure white. The bisulfite ions exercise a protective action on the group or groups in the lignin molecule which cause the brown color. Sulfite waste liquors and lignosulfonic acid which has become dark, can also be made to resume a honey-yellow color by suitable treatment with bisulfite.

Doubt has recently been expressed (57) as to whether the lignin (or in this case the lignosulfonic acid) really changes color under the conditions of the cooking, or whether the change in color is due to the dissolved wood polyoses or their hydrolysis products. E. Hägglund and B. Nelson (58) therefore investigated this point and found that the change in color from yellow to brown or dark brown definitely ran parallel to the decrease in the bisulfite content of the liquor. When spruce holocellulose containing about 1% of lignin was cooked with liquors of various compositions or with pure SO_2 solutions, the liquor remained yellow throughout the cooking. About 30% of the holocellulose went into solution; about 0.6% of this was lignin. When the calcium salt of lignosulfonic acid, prepared through the bis(p-dimethylaminophenyl) methane compound, was heated to 135°C in 5% SO_2 solution it rapidly changed color from yellow to brown or black-brown. A sulfite waste liquor, dark brown in color, was also treated with the "bis" reagent above, and the solution found to be pure yellow after the precipitate had been removed; heating the solution with SO_2 at pH 1 gave no darkening in color even after a long time. Finally, it was found that isolated lignin from spruce, prepared with fuming hydrochloric acid, when heated with bisulfite cooking acid, dissolved initially with a yellow color, which later changed to brown. The dissolved lignosulfonic acid could be completely precipitated with the "bis" reagent, leaving a water-white filtrate.

It may be concluded with certainty that the color change is caused by a condensed lignosulfonic acid.

Of the other methods used for determining the proper time for breaking off the cooking, the test of A. Mitscherlich has probably enjoyed the most widespread use. In this test a test tube, calibrated at $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{24}$, and $\frac{1}{32}$ of the total volume, is filled to the $\frac{1}{32}$ mark with concentrated ammonia. It is then filled with cooking liquor directly from the cooker vent, without cooling. The tube is shaken, and the amount of calcium sulfite read on the scale. This should not be less than $\frac{1}{32}$, if strong pulp is wanted.

It is important that the liquor be drawn from the digester without being cooled. In this way the free sulfurous acid evaporates and only that which is still present as bisulfite, or loosely bound, remains in the solution, and is precipitated by the ammonia. G. Pettersson (59) has shown that this quantity bears a certain relation to the "available calcium."

If the liquor is cooled as it is drawn, the ammonia precipitation gives only the total SO_2 present, provided that sufficient Ca^{++} ions are present; this is of no value in judging when to stop the cooking [cf. Dieckmann (19) p. 192].

A. K ng (60) has proposed a method to follow the course of a sulfite cook by the specific gravity or the refraction index of the cooking liquor. These values depend on the amount of wood substance dissolved in the liquor. They can, therefore, be used to determine the correct time to interrupt the cook in order to obtain the desired grade of pulp.

The course of the cooking process can also be followed by analyzing samples of the pulp, especially for their lignin content.

Several ways of doing this have been worked out in the course of time. If the degree of pulping is to be used as a guide in stopping the cook, only rapid methods are of any use. Among these methods are the color tests, such as the malachite-green test of Klemm (61), for example, in which the pulp is colored a darker green, the higher its lignin content. Another simple method has been described by P. Klason (62). This is based on the behavior toward 80% sulfuric acid of pulp containing lignin. The higher the lignin content, the darker it colors acid. E. Richter, who pulped with 13% nitric acid, estimated the lignin content from the degree of yellow coloring (63). Other qualitative methods for estimating the degree of pulping have been based on the extent to which the lignin is reddened by oxidizing agents (64) such as solutions of potassium dichromate or hypochlorite (see also p. 454).

Another method has been given by H. Roschier (65). A certain amount of pulp is treated with an acid solution of potassium permanganate, and the time is measured (in seconds) until the violet color turns to yellow. The time is naturally shorter for pulps high in lignin.

Instead of waiting for the color change, one can also determine the unused permanganate after a given time (66). This method is probably the one most widely used. The "permanganate number" has a definite relationship to the lignin content and to the "chlorine number" of the pulp (cf. p. 331).

B. SULFITE PULPING WITH OTHER AGENTS THAN CALCIUM BISULFITE

1. Pulping with Sulfur Dioxide. The possibility of obtaining pulp by treating wood with sulfurous acid alone has been considered repeatedly. B. C. Tilghman himself, the inventor of the sulfite process, investigated this problem, and reported (67):

"Several experiments in which wood was treated at high temperatures

and pressures with a solution of sulfurous acid gave fibrous materials which were, however, red, and difficult to bleach. Investigations showed that part of the sulfurous acid had been converted into sulfuric acid, and it appeared that the latter substance had caused the red coloration."

The use of sulfurous acid without the addition of base was also protected in the British Patent No. 385, taken out in 1867, but this did not prevent R. Pictet and G. L. Brélaz (68) from obtaining a patent for the pulping of wood with a 5-7% solution of SO_2 at 80-100° C. However, they did not obtain a completely satisfactory pulp, either. The many other workers who investigated this problem were not much more fortunate (69).

It was long thought that the sulfuric acid in the technical sulfurous acid solution was the cause of the difficulty, and for this reason a quantity of base equivalent to the sulfuric acid was sometimes added. Even then, however, the pulp did not turn out to be sufficiently white, and it required very large amounts of chlorine to bleach it (70).

C. Dorée and A. Hall (71) expressed the opinion that the lignosulfonic acid obtained by this process was a simple and less extensively condensed material than the "complicated" one formed in the usual sulfite process. Actually, however, the solid lignosulfonic acid produced is very much condensed, because of the high acidity, and is therefore difficult to dissolve out. This is also shown by the fact that the lignin is more easily dissolved at the beginning of the cook than later. This phenomenon is quite marked at high cooking temperatures (72).

2. Magnesium, Sodium and Ammonium Salts. C. D. Ekman (p. 414) in his first sulfite mill in Bergvik used a Ca-Mg bisulfite liquor which he prepared from magnesite and limestone. Dolomite was later used for the preparation of cooking liquors in some mills in Europe. The advantage in the use of Ca-Mg bisulfite solutions was chiefly that the precipitation of calcium sulfate and the formation of incrustations was thus prevented. In the course of time calcium bisulfite alone came to be used exclusively but new attempts have recently been made to replace the calcium with other cations whose sulfates are soluble. Mills are already in operation which manufacture sulfite pulp with sodium bisulfite (in Sweden) and ammonium bisulfite (in Norway, and recently also in the United States). The use of magnesium bisulfite seems particularly attractive, because the regeneration is supposed to be especially favorable (73). In some cases the development along these lines has been forced by the fact that the waste liquor may not be let out into the drains from the mill, because it would cause too much stream pollution. In other cases such developments are stimulated by the fact that the organic material can profitably

be used as fuel, if the concentration of the waste liquor can be carried out in a manner sufficiently economical of heat.

Important in this connection is the question as to whether equivalent amounts of different bases have the same effect in the cooking. Investigations by Hägglund and his co-workers (74) indicated that when cooking acids containing equimolar concentrations of Ca and Mg bisulfite were used, the former had a somewhat greater buffering action, and hence a higher concentration of bisulfite ions. The yield of pulp is therefore higher when the extent of delignification is the same, and the yield of sugar is smaller, which is in accordance with the results of Hägglund (cf. p. 419-420).

Ammonium bisulfite has the same effect as calcium bisulfite in equivalent concentration, but unpublished studies by Hägglund indicate that it penetrates the wood more easily.

R. S. Aries (75) recently made comparisons of the quality of the pulps obtained by cooking with bisulfites of Ca, Mg, Na, and NH_4 , and found that the greatest strength was given by sodium and ammonium bisulfite. Magnesium was better than calcium; this was attributed to easier penetration by the magnesium solution.

R. S. Hatch (76), summarizing the results of similar comparisons, states that in the production of pulps of the same bleach requirement the more soluble bases will yield pulp of higher unbleached brightness, there will be a definite reduction in screenings, somewhat lower ether extract, and cooking time may be shortened as compared with calcium base.

C. BEHAVIOR OF DIFFERENT WOODS

1. Wood Character and Pulping. The quality of sulfite pulp depends primarily upon the characteristics of the wood and upon the conditions during the cooking. This problem, so important in the industry, can not be discussed in detail here, but the following important results of recent research may be briefly noted.

Those connected with the pulp and paper industry have long been of the opinion that the wood used has an important influence on the yield and quality of the pulp and paper derived from it. It was often asserted, and correctly, that pulp-making "begins in the forest." There was however, surprisingly enough, complete confusion as to what characteristics of the wood were desirable. Many believed that the morphological characteristics of the fibers were the decisive factor; E. Kirchner, for example, said in his well-known handbook (3, p. 155) that "cellulose with the longest and finest fibers is found in the slender trunks of healthy conifers" and that such fibers impart strength to the paper. Strangely enough, although

this belief was wide-spread, there was no evidence for it in the literature. It was based on purely subjective estimates, and is certainly not generally valid. D. Johansson (77) found for example that sulfate pulp made from Swedish spruce and pine had appreciably higher tensile and bursting strengths than did sulfate pulp from certain American conifers, although the latter had considerably longer fibers.

Systematic studies of this problem have given the following results (78). Spruce grown under widely varying climatic conditions in North, Central, and South Sweden, and under extreme conditions was used. The chief results of the investigations are given in the table on p. 440.

Besides the figures given in the table, the distribution of the fibers between springwood and summerwood was also determined. It turned out that the fast-growing woods (1 to 4) had comparatively few summerwood cells (5-15% of the total number), while the other woods had about 20-30% of summerwoods cells.

The results of the sulfite cooking are given in the table on p. 441. The following conclusions may be drawn from these figures:

The cooking time required to reach a given degree of delignification is about the same for all the woods. When the pulping is carried to the same point, the yield (in per cent of the weight of the absolutely dry wood) is 2-3% less when typical fast-growing wood is used than it is for the other woods. Where the density is 0.4 or more, the yield is constant. This means that while the wood required to prepare a ton of pulp usually remains constant between 4-4.5 cu.m. (1.1-1.3 cords), it can run as high as 6.7 cu.m. (1.85 cords) in the case of fast-growing woods.

The time of beating is undoubtedly dependent on the content of wood polyoses as well on the form of the fibers (79). As far as the strength is concerned, it is evident from these results that extremely fast-growing wood gives sulfite pulps weaker in every respect than those obtained from normal or slow-growing wood.

The lower tearing strengths of the pulps 1-4 is probably due to the fact that the fibers are relatively short and broad. The ratio of length to breadth is here 54, compared to 80 for slow-growing wood.

It has often been asserted that the ratio between length and breadth is the controlling factor in determining the strength. This is a theorem of only limited validity. Woods 11 and 12, with a length-breadth ratio of 89 yielded pulps of high tearing strength, but with average tensile and bursting strength. In the pulp from 14 a, which showed the greatest strength, the length-breadth ratio was 80, but the tensile strength was almost 15,000 m. That the length of the fibers does not alone determine the strength, may be seen from the fact that woods 7 and 8, with average fiber lengths of

A. Physical Properties of Wood Samples

Sample No.	Above (A) or Below (B) the Lowest Branch	Region Where Grown	Type of Tree	Diameter in cm.	No. of Annual Rings	Annual Rings per cm.	Density	Average Length of Fibers (L) in mm.	Average Breadth (Br) of Fibers mm. $\times 1,000$	L Br
1	B	South Sweden	Dominant	44	38	1.7	0.28	2.22	50	44
2	A	"	"	26	18	1.4	0.38	2.49	50	50
3	B	"	"	32	40	2.5	0.32	3.04	48	63
4a	A	"	"	15	15	2.0	0.31	2.64	46	57
4b	A	"	"	15	15	2.0	—	—	—	—
5	B	"	"	25	42	3.4	0.39	3.14	39	81
6a	A	"	"	14	25	3.7	—	2.98	38	74
6b	A	"	"	12	22	3.7	0.41	—	—	—
7	B	Cent. Sweden	"	24	79	6.7	0.39	3.57	45	80
8a	A	"	"	13	39	6.2	0.39	3.42	42	80
8b	A	"	"	12	35	6.1	—	—	—	—
9a	B	"	Co-dominant	18	75	8.3	—	3.18	43	74
9b	B	"	"	18	74	8.3	0.41	—	—	78
10a	A	"	"	11	49	8.9	0.42	3.11	40	—
10b	A	"	"	10	44	8.8	—	—	—	—
11	B	North Sweden	Dominant	21	190	18.5	0.40	3.78	41	92
12a	A	"	"	12	100	17.4	0.42	3.45	40	86
12b	A	"	"	11	90	16.4	—	—	—	—
13a	B	"	Suppressed	16	180	23.2	—	3.35	39	86
13b	B	"	"	16	180	23.2	0.40	—	—	—
14a	A	"	"	11	95	17.3	—	3.19	40	80
14b	A	"	"	11	93	17.7	0.40	—	—	—
15a	B	"	Co-dominant	18	99	11.3	—	2.86	42	69
15b	B	"	"	17	90	10.6	0.40	—	—	—
16a	A	"	"	11	39	7.1	—	2.78	43	65
16b	A	"	"	11	38	7.2	0.39	—	—	—

Sample No.	Total Extractable with Ether and Acetone %	Lignin %	Time of Pulping (hrs.)	Yield of Pulp			Roe No.	Degree of Beating S. R.	Time of Beating (min.)		Tensile Strength m.	Bursting Strength kg. cm ² . (100 g. Sheet)	Tearing Resistance (Elmendorf)
				% of Absolutely Dry Wood	kg. per cu. m. (0.276 cords) of Wood	cu. m. of Wood per ton of 90% Pulp			Actual	Calcd. for 45 S. R.			
1	1.19	29.3	13 ³ / ₄	52.0	146	6.3	4.7	41	70	79	11,800	7.9	62
2	1.40	29.4	12 ³ / ₄	48.5	136	6.7	9.4	43	60	64	12,350	8.3	59
3	0.72	28.7	13 ¹ / ₂	50.9	197	4.6	8.0	40	60	70	12,625	8.6	61
4 a	0.93	28.0	12 ¹ / ₄	53.5	171	5.3	10.6	41	60	68	13,175	8.9	62
4 b	0.96	27.6	13 ¹ / ₂	52.8	169	5.4	7.4	41	65	67	13,425	8.7	60
5	0.88	26.1	13 ¹ / ₂	54.8	170	5.4	10.7	46	70	68	12,700	8.6	54
6 a	1.39	26.3	13 ¹ / ₂	52.1	162	5.6	7.6	44	70	72	13,025	8.2	55
6 b	1.24	27.0	13 ¹ / ₂	54.1	—	—	10.4	44	70	72	12,600	8.0	57
7	2.44	25.9	13 ¹ / ₄	51.8	215	4.5	7.5	43	70	74	12,950	8.0	56
8 a	5.66	26.7	13 ³ / ₄	55.1	220	4.1	7.2	49	55	49	12,650	8.2	70
8 b	2.29	26.2	13 ¹ / ₄	53.4	216	—	6.0	45	55	55	12,800	8.8	76
9 a	1.31	26.6	13 ¹ / ₄	52.6	220	4.4	5.7	44	55	57	12,800	8.6	74
9 b	1.97	27.3	13 ¹ / ₄	56.1	215	4.2	7.3	43	50	53	13,000	9.2	73
10 a	7.04	26.8	14	55.1	212	4.3	8.8	46	50	49	11,900	7.2	67
10 b	1.28	26.8	14	54.5	—	—	7.6	45	50	50	11,400	7.3	71
11	1.56	27.3	14	55.0	—	—	7.5	42	50	55	14,050	10.8	86
12 a	2.22	27.8	14	56.2	231	3.9	7.4	40	50	58	14,300	10.6	82
12 b	2.08	27.2	14	56.4	229	4.0	7.5	42	55	60	11,075	10.1	83
13 a	1.38	28.9	14	54.7	216	4.2	7.1	43	55	59	13,700	9.9	84
13 b	1.50	28.7	14	54.3	218	4.2	7.0	42	60	55	13,650	9.9	76
14 a	1.98	28.7	14	53.9	218	4.2	5.8	41	60	68	12,850	9.0	84
14 b	1.83	28.7	14	52.0	—	—	5.8	40	55	65	12,600	8.5	85
15 a	1.77	27.7	14	52.7	—	—	7.8	41	60	68	11,400	10.7	80
15 b	1.80	27.3	14	53.0	212	4.3	7.4	45	65	65	11,550	10.9	81
16 a	1.79	27.8	14	52.5	212	—	7.3	42	65	71	11,950	10.5	81
16 b	1.44	27.6	14	52.9	212	4.3	8.1	42	65	71	11,275	10.7	74
				53.3	213	—	6.1	45	60	60	14,675	10.3	79
				53.0	—	—	6.1	45	60	60	14,500	10.4	78
				53.1	207	4.4	6.0	41	60	68	13,775	9.7	76
							6.0	43	60	61	14,300	10.1	76

3.5 mm., give appreciably weaker pulp than do 9 and 10, with fiber lengths of about 3.1 mm.

It is obvious then, that the dimensions of the fibers are not the sole factors in determining the strength.

As to the forestry conditions, it was found that the pulps having the greatest strength came from co-dominant or suppressed trees in Central or Northern Sweden.

This circumstance has stimulated investigation into the manner in which forest cultivation should be conducted, especially with reference to the effect of intermediate cutting on the quality of the wood.

Representative samples of normal spruce wood were obtained from sample plots which were supervised with professional skill and were distributed throughout the country (80).

The very extensive investigations revealed that the variations in yield and quality of the pulp obtained from wood from the same plot were nearly as great as the total range of variations among all the samples of wood. It also turned out that the variations in the same trunk were unexpectedly large.

The yields of pulp must be considered in connection with the extent of delignification. At a Roe chlorine number of 6, the average yield from all samples was 50.6%. The averages of samples from the outer, medium, and inner parts of the trunk were 50.4, 50.8, and 50.1%, indicating that thinning has little effect on the yields. It was found, however, that top logs gave 2% lower yields than butt logs. The strength of the pulp varied even more than the yield, the position of the wood in the trunk having a small but definite effect. Pulp made from wood from the inner part of the trunk showed greater tensile and bursting strength than that made from wood from the outer parts. The opposite was true of the tearing strength. These differences disappear toward the upper end of the tree.

Statistical analysis of the results showed that there is no connection between the percentage of summerwood present and the strength of the pulp; the breadth of the annual rings also appears to have no effect.¹

¹ *Note added in proof.* A similar investigation of the relationships between the growth conditions and the properties of Swedish spruce wood and its sulfite pulping characteristics has been carried out during the last years at the Swedish Forest Products Research Laboratory in cooperation with the Forest Research Institute of Sweden. This investigation which is based on considerably more material than those referred to above (79, 80), has, on the whole, confirmed the results previously obtained. Spruce of different branching type, such as "comb"-spruce, "flat-branched" spruce, spruce with ribbon-like or with broom-like branches, showed no difference in pulping behavior, provided that growth conditions were similar. Furthermore, it was shown that tensile, bursting and tearing strengths are lower for pulps from top logs than for pulps from butt logs. It was also found that the further north the tree came from the lower was the yield and the tearing strength of the pulp obtained. On the other hand, bursting and tensile strengths showed the reversed behavior.

Similar investigations of certain American woods have been carried out by G. H. Chidester, M. W. Bray, C. E. Curran, J. N. McGovern, and G. C. McNaughton (81). According to them, the content of spring- and summer-woods in the wood is quite significant for the yield and quality of the pulp. Curran found that fast-growth woods having a high percentage of springwood and, on the other hand, slow-growth woods having a low springwood content give pulps with high bursting strength, and that the tearing strength increases with the proportion of summerwood. Chidester, McGovern, and McNaughton investigated "loblolly," "shortleaf," "longleaf," and "slash" pines, and found that the thin-walled fibers of springwood tend to collapse, giving ribbon-like fibers which form a smooth and dense paper. The tensile strength appears to decrease with increasing amounts of springwood, while the bursting strength and folding endurance increase (82). *

2. Sulfite Pulping of Pine and Other Woods. By far the largest part of the sulfite pulp is made from spruce wood. Because of the enormous increase in the production of sulfite pulp the time eventually came in many countries when not enough spruce could be obtained from the native forests. Attempts have been made for a long time, therefore, to use other soft woods for the production of sulfite pulp. The interest in pine has been particularly great.

It has long been known that the various parts of the pine trunk, i.e., the heartwood and the sapwood, behave quite differently toward ordinary sulfite cooking liquors. E. Kirchner, for example, reported in 1901 (83) that heartwood of pine exhibits a great resistance toward sulfite pulping liquor; as a result, pine wood has been very unpopular for the fabrication of sulfite pulp. Kirchner attributed the behavior of the pine to its high resin content. He reported that the sapwood was usable, however, and several factories succeeded in pulping so-called "slabs" from sawmills.

The idea has been quite wide-spread among experts that the difficulty in pulping pine wood is due to its high resin content, although this fact has not been proved experimentally. C. G. Schwalbe, indeed, totally rejected this viewpoint after he had found that heartwood of pine which had been extracted with benzene or ether could still not be pulped with sulfite liquors (84). He offered a quite different explanation, for he had found that wood chips which had been stored for many years could not be pulped in the usual way. He also believed that he had established the fact that green wood could be pulped more easily than ordinary dry wood.

To explain these facts, he assumed that the greater difficulty in pulping was due to drying and coagulation of plant juices; such drying could also be caused by treatment with benzene or ether. A similar process was assumed to occur in growing trees, with the passage of time, with the result that the older parts of the tree, particularly the heartwood, had been subjected to a harmful aging. This would explain why the heartwood could not be pulped in the normal way.

This explanation could not, of course, hold for all kinds of wood, for it had been proved that the heartwood of spruce could be pulped just as easily as the sapwood (85).

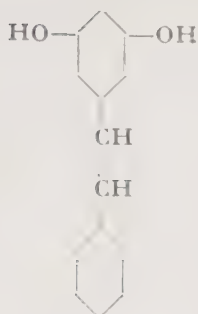
It turned out also, that benzene and ether did not cause an "artificial aging." Heartwood of pine could not, it is true, be pulped after extraction with these solvents, but if the wood was then further extracted with alcohol or acetone, the sulfite pulping process could be initiated easily, and proceeded as smoothly as the pulping of pine sapwood or of spruce (86).

This fact indicated that the alcohol or acetone extract must contain a material which impeded or prevented the pulping, but it did not reveal what this substance might be. It was possible that certain resinous materials were so distributed in the heartwood that they stopped up the pores and thus prevented the pulping liquor from penetrating wood. Such a view was expressed by C. G. Schwalbe and A. af Ekenstam (87) for example.

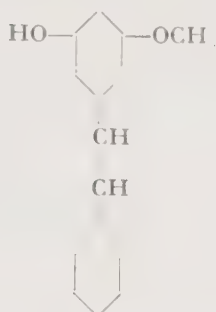
Colloid-chemical points of view have nevertheless maintained themselves until very recent times (88). According to these views, the fact that pine heartwood which has been extracted with alcohol or acetone can be pulped was explained by saying that the wood swelled when it was treated for a long time with steam to remove the solvents after the extraction. Only for this reason did the removal of the resin help the pulping; the resin of pine actually did not hinder the sulfite pulping any more than did the resin of spruce.

This explanation overlooked the following point. It had been shown that the material extracted did not hinder the sulfonation of the lignin, but did have a decided effect on its dissolution. It was further shown that the disturbing substances were neither fatty acids nor resin acids, but quite different materials (89).

The chemical constitutions of these substances were investigated in Hägglund's institute by H. Erdtman (90), who found that two different substances were involved, 3,5-dihydroxystilbene (I) and its monomethyl-ether, 3-hydroxy-5-methoxy-stilbene (II).



I Pinosylvlin



II Pinosylvlin Monomethylether

The first was called pinosylvlin (after *Pinus silvestris*) and the second would then be pinosylvlin monomethylether. A total of 0.8% of these compounds could be isolated from heartwood of pine (cf. also p. 343). The presence of heartwood in mixtures with sapwood can be conveniently demonstrated by reactions given by the pinosylvlin phenols, e.g., the red color developed with diazotized amines such as benzidine (91) or the bright blue fluorescence, which appears on irradiation with ultraviolet light (92).

Both compounds are easily soluble in ether, but the larger part of them nevertheless remains behind in the wood when it is extracted with ether. This is not caused by a strong absorption of the compounds by heartwood, for heartwood which had been extracted with acetone and then impregnated with an acetone solution of pinosylvlin gave up the pinosylvlin readily on washing with ether. The explanation is rather that the pinosylvlin and its monomethyl ether are locked up in the cells or cell walls in a layer which is insoluble in ether, but soluble in acetone and alcohol (93). This theory is supported by the fact that if powdered heartwood of pine is extracted with ether and then with acetone, and the acetone extract concentrated and treated with ether, a voluminous precipitate appears, which evidently consists of the ether-insoluble layer postulated above. This layer is evidently removed by acetone or alcohol, for if pine heartwood is exhaustively extracted with ether, moistened with a small quantity of acetone or alcohol, well dried, and then extracted again with ether, the pinosylvlin goes into solution. The layer which prevents the dissolution of the pinosylvlin could also be destroyed with water (after extraction with ether) but not nearly to the same extent as by treatment with alcohol or acetone. These investigations also explain the results of E. Hägglund, J. Holmberg, and T. Johnson (89), who found that the amount of material which can be extracted from heartwood of pine varied with the state of subdivision. When it is very finely ground, the ether-insoluble layer is in part destroyed mechanically.

Now, how do the phenols of the heartwood behave during the sulfite pulping of pine?

If the content of phenols is followed through the sulfite cooking process, it will be found that the phenols have disappeared by the end of the pulping. They are evidently condensed with the wood residue, for oxidation of the residue with potassium permanganate yields benzoic acid, as does pinosylvin.

In this connection it should be emphasized that the deleterious effect of pinosylvin has no connection with the fact that it is a stilbene derivative, for as Erdtman showed, stilbene itself does not disturb the pulping at all. The effect is due entirely to the phenolic groups. Different phenols have quite different effects, to be sure; ordinary phenol has only a slight influence on the pulping, as does pyrocatechol, but pyrogallol, phloroglucinol, orcinol, and resorcinol retard the pulping greatly. The effect is therefore obviously dependent on the reactivity of the phenol.

It is a well-known fact of lignin chemistry that phenols and similar substances react easily with lignin in acid solution (cf. p. 246). This would mean that the pinosylvin-lignin condensation product would be difficultly soluble, or under certain circumstances, impossible to dissolve out (94).

On the other hand, earlier investigations had shown that heartwood of pine was easily pulped by relatively strong solutions of NaHSO_3 , or by magnesium bisulfite solutions with high base content (86). If the ideas presented above are correct, this would mean that in such cases the condensation with phenols was diminished or excluded completely.

This actually proved to be the case. A 15% sodium bisulfite solution has a pH of 4.5 at room temperature. Ordinary sulfite pulping liquor is about one hundred times as acid. When 40 g. of spruce wood was heated to a maximum temperature of 130°C with 200 cc. of this sodium bisulfite solution in the presence of 1.1 g. of resorcinol, and then ground and carefully washed with water, a 94% yield was obtained of a material with a sulfur content of 0.96%. This material was pulped with ordinary sulfite cooking liquor, and the pulping was found to proceed in a completely normal fashion. The lignin had evidently not reacted with resorcinol to any appreciable extent under these conditions (94).

It follows from these and from other experiments that the acidity is the controlling factor in the reaction between phenols and lignin.

The reaction with phenols becomes important only when the cooking liquor is sufficiently acid, and when the temperature is raised rapidly. When care is exercised to keep the acidity moderate, as it is in NaHSO_3 solutions, for example, then the lignin takes up chiefly sulfite, but no phenol. After the sulfonation of the lignin has occurred, the pulping

proceeds quite normally, even when usual, highly acid bisulfite cooking liquors are employed to finish the cooking (cf. p. 207).

It is also quite advantageous to carry out the initial sulfonation in neutral or slightly alkaline solution, and then to dissolve out the ligno-sulfonic acid with highly acid bisulfite-sulfurous acid solutions. J. A. Graham (95) patented such a procedure at an early date. It has been proposed for the pulping of heartwood of pine (96).

B. O. Lindgren (97) has been able to imitate the competition between sulfonation and phenol condensation using vanillyl and veratryl alcohols as model substances.

It is remarkable that such small quantities of phenol can have so marked an effect in hindering the pulping. H. Erdtman found, for example, that 1 mol. of resorcinol can react with six lignin units (average molecular weight = 178) in the normal sulfite cooking. This prevented more than 50% of the lignin from being brought into solution. Pinosylvins are still more effective; this must be due to the difficult solubility of the pinosylvins as they are found in the cell walls, beneath the acetone-soluble layer mentioned above.

The formation of condensation products between lignin and phenolic constituents during the sulfite cook is not confined to pine heartwood. As J. C. Pew (97a) has shown, heartwood from Douglas fir contains taxifolin (3,5,7,3',4'-pentahydroxyflavanone) which inhibits the sulfite digestion of this kind of wood.

The question may be asked here as to whether the resin content of the wood really does not retard the pulping. The answer is that it does under certain circumstances. E. Hägglund and F. Hedborg found (98) that when slow-growth heartwood of pine, containing much resin, was pulped by the two-stage process, using sodium sulfite in the first step, and sodium bisulfite- SO_2 solution in the second step to dissolve the lignin, the solution of the lignin proceeded extremely slowly. Burnt cook occurred before the pulping had gone far enough. Once this phenomenon appears, the yield of pulp diminishes, but the lignin content does not decrease.

It is questionable, to be sure, whether this negative result is due entirely to the resin content, although this was certainly high (10% ether-extractable + 1.2% acetone-extractable). E. Hägglund and S. Larsson (99) as well as H. Erdtman (100) investigated the sulfite pulping of spruce branches, which contained no less than 15.1% of total extractables, and found that they could be pulped very well by the two-stage process. Erdtman reports that the phenol fraction of the resin from these branches contains no phenols which retard the pulping strongly. It would thus appear that the inhibition of the sulfite pulping in heartwood of pine

with a high resin content is due to the fact that the resin so reduces the permeability of the cell wall that the lignin reacts with pinosylvin before sufficient sulfonation has occurred. [For the cause of the change in the permeability on heartwood formation, see R. Trendelenburg (101)].

Finally, studies were also made to determine whether the density of the wood really had any great effect. For these investigations wood from a spruce pole thicket was used. Trees from such stands have, when 100 years old, a diameter of only 5-6 cm. at the ground. The wood was therefore exceptionally dense (density = 0.54), but despite this fact it could be pulped without difficulty (100). It may be concluded that extreme slow growth of a wood has no great effect on its behavior during sulfite pulping.

The phenomena appearing in the sulfite pulping of pine heartwood have their parallels in the case of lignin which has been condensed without the aid of phenols. It is well-known that wood which has been treated with acid is difficult to pulp with sulfite liquors. The same thing is true of isolated lignin, which is always more or less altered or condensed.

3. Sulfite Pulping of Hardwoods. Compared with softwoods, hardwoods possesses short fibers, which makes them less suitable for paper pulp manufacture. In spite of this and other disadvantages extensive work has been done to make hardwoods available for sulfite pulping, especially for the manufacture of rayon pulp, where fiber length is an unimportant factor. In Germany, rayon pulp was made from beech [cf. G. Jayme and E. Lochmüller-Kerler (102)]. Investigations on sulfite pulping of birch wood, which gave satisfactory results have been reported by E. Hägglund, W. Améen, T. Berge, I. Lindholm, and H. Nihlén (103). The dissolution of the last parts of lignin was more difficult than in spruce, but the bleached and refined pulp seemed to be suitable for the conversion to viscose rayon. G. A. Richter (104) comes to the conclusion that hardwoods as white and yellow birch, beech and maple, especially when pulped with sodium base liquor, yield a pulp that possesses value in the paper industry, and experiments, mentioned by M. W. Bray (105) indicate that conventional pulping procedures are satisfactory for pulping such hardwoods as black willow, Southern cotton wood, sugarberry and swamp tupelo.

W. Lautsch (105 a) has studied the influence of pre-hydrolysis of wood on the delignification by the sulfite process. He treated beechwood with 0.5-1.5% aqueous sulfurous acid, potassium chloride-hydrochloride acid solution (pH 1.22), or lignosulfonic acid solution (pH 1.2) at 105°C; or with 2% solutions of formic, acetic, or propionic acid at 135°C, or with water at 150°C. The wood residues were successively heated at 135°C with

magnesium or sodium bisulfite solutions of pH 5-7 for 8 hours, and then with cooking acids of lower pH for 6 additional hours.

The pulp yields varied between 40.7 and 47.8 percent, the DP between 550 and 1,060, and the pentosan content between 6.4 and 10.6%. The best results were obtained when the wood was heated with a 1.5% solution of sulfur dioxide (wood liquid ratio = 1 : 20) for 3 hours at 105°C. The residue, which amounted to about 70% of the wood weight, was then pulped at 135°C with 0.5 *M* sodium sulfite of pH 6 for 8 hours and thereafter with a solution containing 5% SO₂ and 0.9% NaOH for 6 hours. The yield was 41.7%, and the pentosan content of the pulp 6.9%. It is obvious that prehydrolysis of beechwood did not bring about any change in the lignin which inhibited the sulfite pulping.

D. PROPERTIES OF SULFITE PULP

1. Pulping Conditions and Pulp Properties. The strength of the pulp is determined not only by the wood but also by the cooking process. The changes in strength which occur during the normal cooking process are of great importance. The curves of Figs. 74 and 75 show how the strength of the pulp varies with different degrees of pulping. In these experiments chips of quite different dimensions were employed, ranging from 8 to 40 mm. in length and from 4 to 12 mm. in thickness (106).

The strength of the pulp is also very much affected by the composition of the cooking liquor. The following figures give some information about this point:

Ratio of Cooking Acid to Wood, 5:1. Total SO₂, 5 g. per 100 cc.
Final Temperature 125°C

Lime Content g. CaO/100 ml.	Roe Number	Time of Beating in Lampen Mill to 45° S. R. (min.)	Strength Characteristics				Average Whiteness in % of Blanc Fixe
			Tensile Strength (km.)	Stretch %	Bursting Strength kg./cm. ² 100 g. Sheet	Tearing Resistance (Elmen- dorf)	
0.60	9.6	58	13.6	5.5	10.0	70	69
1.00	10.3	55	14.0	5.6	10.8	70	75
1.40	10.5	47	15.3	6.1	11.3	71	77
0.60	5.5	67	13.1	6.4	10.1	70	74
1.00	4.8	51	13.7	6.2	10.6	71	79
1.40	6.3	64	14.9	6.0	11.2	73	81

It is particularly important for the maintenance of strength that the wood shall not be disintegrated during the cooking, since, as was found by Hägglund (107), isolated fibers are strongly attacked by cooking liquor; this fact has been confirmed in large scale operation. When rotating digestors are used, it is almost impossible to avoid some disintegration

into fibers. For this reason it is not advisable to use rotating digesters for the manufacture of sulfite pulp of low lignin content, if the highest possible strength is desired.

The susceptibility of the isolated fiber to sulfite cooking acid (as well as to alkaline liquors, cf. p. 482) is also demonstrated by the fact, that damage caused during chipping of wood which had been heated in water preparatory to drum barking and chipped while still hot, results in a pulp

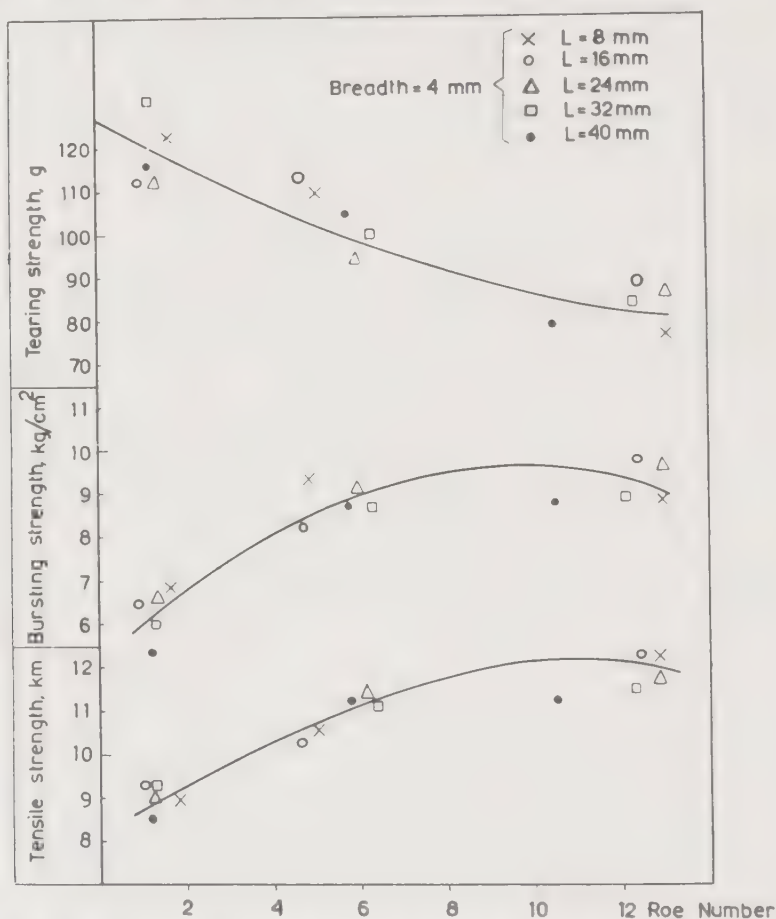


Fig. 71. Strength characteristics as functions of the degree of delignification of sulfite pulps prepared from wood chips of varying lengths (L).

with diminished strength (108). The effect of chipping was confirmed by H. Green and F. H. Yorston (109) and by C. A. Anderson (110), who found considerable loss in pulp strength due to the bruising action of a chipper knife. Hand made chips gave exceptionally high-strength pulp. Abnormally weak pulp was also obtained from crushed or hammered wood (111). If the wood has been disintegrated to fibers before pulping, the pulp will consist of worthless fiber fragments (107). Further, pulps of

diminished strength characteristics are obtained, if the wood has been exposed to high compressive stresses (112).

The reason for this specific effect is not yet fully understood. The strength of the isolated fiber doubtless depends on the acidity of the liquid surrounding it during the pulping. Since the fibers incorporated in the wood are not usually damaged during the cooking, one must conclude first of all that the outsides of the fibers, which are not exposed in the

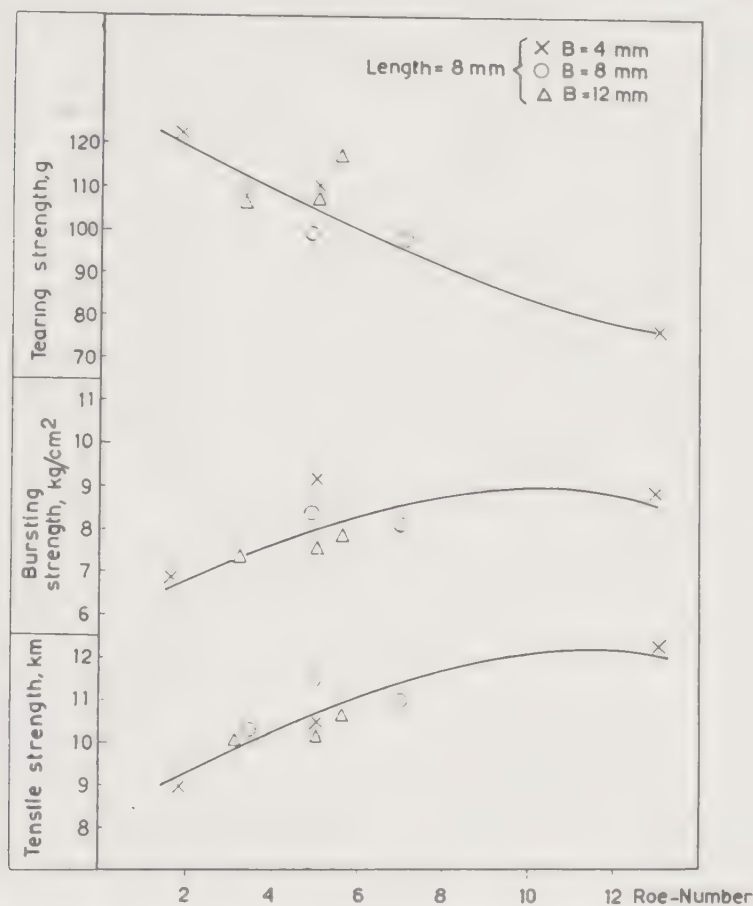


Fig. 75. Strength characteristics as functions of the degree of delignification of sulfite pulps prepared from wood chips of varying breadths (B).

intact wood, determine the strength. Furthermore, in this part of the fiber—the primary wall—the acidity during pulping must be very slight compared to that of the cooking liquor. This does not at first seem probable, but it can be understood in view of the fact that the lignin which occurs abundantly in the compound middle lamella can rapidly tie up the acid which enters, by binding it as sulfonate.

G. Jayne and L. Grøgaard (113) believe that the cellulose in the wood

cells is protected by surrounding lignin [cf. the wood fiber model of K. Freudenberg and W. Dürre (114), modified by Jayme and co-workers (115) and by H. Dolmetsch (116)].

Experiments have been undertaken by G. Jayme and E. Lochmüller-Kerler (117) with a view to determining the connection between the chemical composition, the yield, and the strength of pulps. For this purpose beech wood was submitted to a mild sulfite pulping, and the partly delignified pulp thus obtained was bleached with sodium chlorite. The sulfite pulp so produced had only a low strength; this fact was attributed to the high content of lignin and wood polyoses. The change in strength

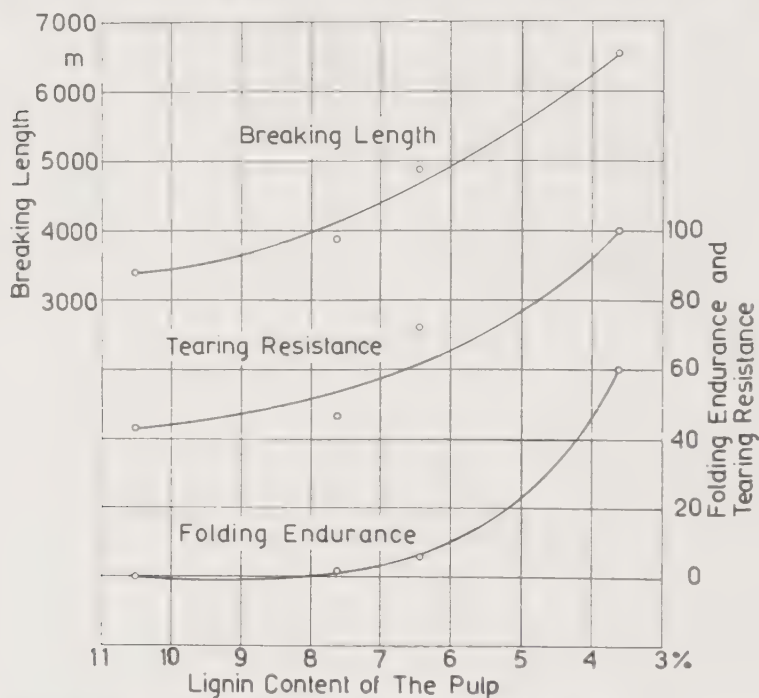


Fig. 76. Changes in the strength characteristics of a beech sulfite pulp on bleaching with NaClO_2 .

was therefore determined when the pulp was gradually treated with sodium chlorite to remove the lignin. The results are shown in Fig. 76. It was possible to conduct the bleaching in such a way that the strength of the bleached pulp was about 15% higher than that of the unbleached pulp (118). Too high a content of polyoses has an unfavorable effect on the strength; the maximum strength comes with an optimum polyose content. When the polyoses are removed from a pulp whose yield has exceeded the optimal yield, the average strength is raised; if the pulp yield was less than the optimum, the strength is lowered.

According to these results, the maximum strength is obtained under

the following conditions: freedom from lignin, optimal content of wood polyoses, and an unchanged degree of polymerization. [For the connection between the length of the cellulose molecule chains and the strength of the fibers, see H. Staudinger (119)].

The pulps from different woods contain celluloses with about the same degree of polymerization, according to H. Staudinger (120) even if different methods of pulping are used. Staudinger believes that the varying behavior of pulps produced by the sulfite and sulfate processes depends in part on certain constituents, especially the wood polyoses, which occur in different amounts.

Pulps are often characterized by their α -cellulose contents (cellulose insoluble in 18% NaOH) by which Staudinger understands cellulose with an average degree of polymerization of more than 200 (122). The α -content can vary widely, according to the method of pulping (123).

According to H. Dolmetsch and F. Reinecke (121), the average degree of polymerization (DP) of refined sulfite celluloses containing over 96 % α -cellulose is 1200-1800, and that of paper celluloses containing 85-92 % α -cellulose, 800-1300.

The average degree of polymerization (DP) of a pulp is decreased in the processes used to make films or fibers from it. The rayons produced by the viscose process frequently have a DP of 300-400, and efforts are often made to increase this number. Fibers made by the cuprammonium process usually have a higher DP, running around 400-500.

As far as the strength of the pulp is concerned, it is not necessary to have a particularly high DP, as long as it is kept above a certain limiting value (about 700) (124).

For a discussion of the change in strength caused by chemical degradation of the cellulose, the reader is referred to p. 117.

More or less extensive changes in the properties of pulp can be caused by mechanical means. According to H. Staudinger and E. Dreher (125), beating in a Hollander beater does not change the DP of the cellulose, but grinding in an agate ball mill causes strong degradation (cf. p. 117).

In this connection the content of "flour" in the pulp should be mentioned. Investigations by O. Wurz and O. Swoboda (126, 127) have shown that the size of the chips used for the cooking has no great influence on the extent of the occurrence of flour-like particles in the pulp. No direct connection between the content of flour and the extent of delignification was discovered, either, but a large amount of such material was obtained in pulps of low viscosity. When the flour-like material was separated with a special screen, the pulp acquired increased water absorption capacity, lower ash content, and extremely low contents of rosin and fat. Pulps

containing flour had higher tensile strength than pure long fiber pulps.

The composition of the flour-like constituents and its influence on the viscose rayon process were examined by F. Wultsch (128). The flour contained medullary ray cells rich in rosin and disturbing in the production of artificial silk. It also contained fragments of fibers, which arise mechanically during the process but are harmless in further chemical processing, as well as ash-forming impurities. Washing out the flour increased the α -cellulose content, and caused decreases in the alkali-soluble material and the ash. The copper number and the wood gum content did not change. Flour in the pulp causes turbidity and poor solubility during the production of viscose solutions.

2. Reddening of Pulp. Treatment of unbleached pulps with oxidizing agents, such as hydrogen peroxide, for example, causes a more or less pronounced red coloration of the pulp. Pulps which have been stored in contact with the air for some time become red on immersion in NaCl solution. This phenomenon has been the subject of repeated studies by various investigators. The work of E. Heuser and S. Samuelsen (129) should be mentioned in this connection. They found that the red color is probably caused by the lignin. O. Aschan (130) thought that there was present an organic dyestuff which perhaps had something in common with the lignin. The investigations of H. E. Wahlberg (131) showed that the color had something to do with iron and copper compounds in the pulp. The color could be removed to a certain extent by the addition of sulfurous acid; this was sometimes attributed to a reduction process caused by this acid (132).

E. Hägghund and E. O. Hedman (133) showed that the red color was due to the lignosulfonic acid present in the pulp; hence the effect is most pronounced in pulps of high lignin content.

If spruce wood is heated with neutral sodium sulfite, the solid lignosulfonic acid formed does not give a red color on oxidation. The wood itself is also not colored when it is oxidized. Only after the action of acid, e.g., heating for an hour at 120°C with 0.25% sulfuric acid, does the red coloration appear on oxidation with 3% hydrogen peroxide.

It may be concluded from this that the acidity of the sulfite cooking liquor plays a decisive part. Sulfite pulp sometimes gives with ferric chloride a greenish color which turns to violet, when ammonia is added. These color reactions are characteristic of pyrocatechol derivatives. Since the red color caused by oxidation is also relatively unstable, it is tempting to assume that an *o*-quinone is present. Pulping with bisulfite might then, to a certain extent, give rise to the formation of groups of the pyrocatechol type in the lignosulfonic acid (133, 134).

Another possible structure of those groups in oxidized lignosulfonic acid, which are responsible for the red color, is that of a stilbene quinone (134 a).

The oxidation which leads to red coloration has been found to be accelerated by copper especially. Even very small amounts of copper are sufficient to cause a strong effect, which is enhanced by the tendency noted earlier (135) of sulfite pulp to undergo rapid cation exchange. Metal once taken up by the pulp remains there, and can not be removed by washing in the factory. When care is taken that no copper comes into the process, the oxidation proceeds so slowly that it appears as if the pulp had lost its ability to become red. This is not the case, however.

E. Hägglund, B. Fehrm, and L. Waenerlund (136), following the earlier work of O. Aschan, have investigated the possibility of decreasing the tendency toward reddening. This can be done by treating the freshly manufactured pulp with solutions of bisulfite and hyposulfite. Such treatment does not guarantee, however, that a red coloration will not appear after sufficiently long standing.

As E. Adler and S. Häggroth (136 a) have shown, the reddening is also inhibited when the heavy metal ions present in the pulp are bound by complex-forming substances, such as ethylenediamine tetraacetic acid, hexametaphosphate, and pyrophosphate.

Instead of protecting the groups in the lignin which are responsible for the red color, it is possible to destroy them; this is done quite easily by a slight chlorination of the pulp. The red color caused by this treatment is easily removed by SO_2 solution, and the pulp processed in this way shows no tendency to revert to a red color (136).

3. Fluorescence of Pulp. When sulfite pulp is illuminated with ultra-violet light a strong violet fluorescence appears (136 b). E. Hägglund, T. Johnson, and L. H. Trygg (56) observed that this fluorescence is diminished when the pulp is treated for a short time with dilute sodium hydroxide, acidified with dilute acetic acid, and washed with water. Since treatment with alkali is known to remove the loosely bound sulfurous acid, it was believed that the bright fluorescence might be due to carbonyl groups combined with sulfurous acid. In fact, the fluorescence was increased again, when bisulfite solution was allowed to act upon the alkali-treated pulp.

Sulfite waste liquors and isolated lignosulfonic acids behave quite similar to sulfite pulps. In addition, it has been found (136 c) that the fluorescence of lignosulfonic acid solutions disappears on treatment with the aldehyde reagent dimedone. This was, however, not true in the case

of sulfite pulp. It was also found that coniferaldehyde and its methyl ether do not behave like lignosulfonic acid or sulfite pulp with respect to their fluorescent properties. The chemical nature of the fluorescent groups is, therefore, still obscure.

III. By-Products of Sulfite Pulp Manufacture

The by-products of sulfite pulping consist of a number of volatile products derived from the wood as well as of large quantities of lignin and of sugars dissolved in the waste liquor. Most prominent among the former are acetic acid, formic acid, methanol, and cymene.

A. VOLATILE BY-PRODUCTS

W. E. Cross (137) proved, among others, that acetic and formic acids arise on gentle hydrolysis of lignified materials. Even at 110°C these acids were split off by the action of 1% sulfuric acid. Cellulose gave neither of them under the same conditions. When fir wood was used, the ratio of acetic acid to formic acid was 4:1.

M. Hönig (138) determined the amounts of acetic and formic acids in sulfite waste liquors, and found that they could vary widely. One liter of liquor gave from 2.151 to 9.078 g. of volatile acids, calculated as acetic acid. No other volatile acids were present besides acetic and formic. The ratio of acetic to formic acid ranged from 6:1 to 14:1.

Later investigations have shown that the yields of formic and acetic acids are considerably smaller on the average than was formerly assumed. The following analyses of sulfite waste liquors are of interest in this connection (139).

Cooking Time in hrs.	Tempera- ture in °C	Loosely Bound SO ₂ g./100 g. Wood	Formic and Acetic Acids g./100 g. Wood	Yield of Pulp g./100 g. Wood	Color of Liquor
6	110	0.96	2.08	85.8	Colorless
9	116	1.83	2.10	76.0	Yellow
15	133	3.68	2.25	49.5	Yellow
17	135	3.79	2.45	47.0	Brownish yellow
18	135	3.52	2.50	45.2	Dark brown
19	135	3.52	2.50	43.3	Black

It may be seen from the table that an appreciable part of the acetic acid is split off during an early stage of the cooking.

As has already been mentioned (p. 319), the acetic acid which is formed by the action of acids or bases on wood comes from the carbohydrates rather than from the lignin. The assumption (140) that the acetic acid is bound to the lignin molecule as a hemiacetal is therefore incorrect.

Acetic acid is rather easily split off from hardwoods on cooking with dilute acid. This is, however, hardly the reason why hardwoods are said to require cooking liquors richer in sulfite (141).

Considerable quantities of carbon dioxide are also formed during the cooking. This fact was first established by O. Giller in 1925 (142). Thorough studies of this phenomenon led to the result that the carbon dioxide formed during the cooking amounts to about 1.5% of the weight of the pulp. O. Routala (143) and his co-workers have taken up the question of the formation of carbon dioxide, and found that it comes from the aldonic acids in the waste liquor. The action of sulfite pulping liquor on calcium gluconate yields carbon dioxide and a pentose.

Methyl alcohol is also formed as a by-product of sulfite pulping. It probably originates from methoxyl-containing carbohydrates (cf. p. 285). H. Bergström (144) found that pulping of Swedish spruce gave quantities of methyl alcohol running up to about 7 kg. per ton of pulp. This corresponds to about 4 kg. per 1,000 kg. of wood, or nearly 1.5% of the weight of the lignin. Most of the alcohol remains in the waste liquors, only about a third passing off with the gases. The remainder appears only when the liquor is fermented and worked up for ethyl alcohol (145).

During sulfite cooking, terpenes give rise to cymene, which is the main constituent of the so-called "sulfite turpentine," which can be recovered by condensing the volatile vapors occurring in the relief gases of the digester.

P. Klason (146) was the first to show that this oil consisted chiefly of p-cymene, and not of terpenes, as had previously been assumed. A. W. Schorger (147) reports that the yield in American mills amounts to 0.36-1.0 gallons per 1,000 kg. of pulp, while O. Aschan (148) in Finnish mills obtained 0.5-1.5 kg. of cymene per cu. m. of wood (0.28 cords), which is appreciably more. In Sweden the experience has been that less cymene is usually recovered, the yield amounting to less than 1 kg. per ton of pulp (149).

The varying yields of cymene are naturally due to the fact that the terpene content of the wood depends on the treatment it has received.

Investigations by Z. Kertész (150) have shown that the crude oil consists of 80% cymene and 20% of dipentene and sesquiterpenes. O. Aschan also found that the crude oil contained large amounts of materials other than cymene, including probably methylfurfural and sesquiterpenes.

Several workers have studied the crude oil since then. E. Boedtker (151) found, in addition to p-cymene and terpenes, small amounts of fatty acids, resins, and methylfurfural. O. Routala and A. Pohjola (152) found that 74-81% of the crude oil consisted of p-cymene, the remainder

containing sesquiterpenes and in some cases dipentene, borneol, fatty and resin acids. These workers made an interesting attempt to explain the formation of cymene.

They found that sulfur and sulfite cooking liquors could convert pinene to cymene only in the presence of wood chips. They suggested, that terpenes are converted to cymene by the oxidizing action of the sulfurous acid, in accordance with Hägglund's theory of aldonic acid formation (cf. p. 431):



The opinion was expressed that the pinene is converted to cymene by the following route:



H. Wienhaus (153) assumes that the native resin acids of the wood are also altered during sulfite pulping. By splitting off CO_2 , CO , and H_2O they can be converted into hydrocarbons.

B. UTILIZATION OF WASTE LIQUOR

The manufacture of ethyl alcohol is now a special part of the operation of many sulfite pulp mills, especially in Scandinavia and Germany. This use of the sulfite waste liquor is obvious, but cannot be carried out profitably in all cases, especially when the pulp production is too small. A detailed description of the process will not be given here [cf. E. Hägglund (145)]. For recent developments in the United States and Canada, see references (154, 155).

The profitable operation of the plant requires in particular that fermentable sugars be obtained in the liquor in as high a concentration as possible. The formation and the destruction of sugar (cf. p. 430) during the cooking are the controlling factors here.

The yield of alcohol depends partly on the lime content of the cooking liquor and partly on the extent of delignification; a lower lime content and greater delignification lead to higher yields of alcohol. Therefore, at a given degree of delignification, more alcohol can be obtained from the waste liquor if the lime content of the cooking liquor is decreased. Of course, this also leads to reduced yields of pulp and lowered strength. The reason for this is partly that the available base is used up before the cooking is completed, and the acidity of the cooking liquor therefore increases. Hence the idea arose that it might be possible to improve the properties of the pulp by cooking with small amounts of lime, and in two stages. This scheme has been suggested in the NAF-Hägglund process (156). The

first stage is so arranged that the available lime is completely consumed; this gives a liquor having a high content of sugar. The liquor is then drawn off, and new cooking acid is added, the lime content being so arranged that an increase in acidity during the later stage of the cooking is avoided. At least 75% of the first-stage liquor has to be drawn off in order to avoid catalytic decomposition of the second-stage cooking acid by the sugars remaining from the first stage (cf. p. 425). The proper composition of the acid depends on the extent of delignification desired; if an easy bleaching pulp is wanted, one can use a very low lime content in both stages, and thereby double the yield of alcohol. It may be said in summary, that the multi-stage process yields considerably more alcohol than the one-stage process, when pulps of equal strength are produced.

A statement of C. R. Bergson (157), according to which equally high yields of ethanol could be obtained in a one-stage process, giving stronger pulp at the same time, has been doubted by D. Johansson (158). The latter author (159) has also studied the conditions for a maximum alcohol production, pulping at a low lime content and high final temperatures, whereby low strength pulps were obtained.

The neutralization of the waste liquor preparatory to fermentation serves a double purpose, viz., to remove unused sulfurous acid and to adjust the pH to a value suitable for the yeast cells. It is usually performed by addition of chalk or of lime sludge, a by-product from the sulfate pulping process, at a temperature of 80-90° C, the final pH value being about 5. The removal of sulfurous acid is necessary because this substance would decrease the ethanol yield chiefly by tying up the acetaldehyde which is formed as an intermediate in fermentation. As previously mentioned (cf. p. 429), there are only small amounts of free SO_2 and bisulfite ions present in the waste liquor, the bulk being combined with carbonyl compounds as "loosely bound" SO_2 . As this is in equilibrium with free SO_2 (p. 430), it will interfere with fermentation in the same way as free SO_2 . This is easily understood if one considers that the acetaldehyde bisulfite addition compound is only slightly dissociated into acetaldehyde and bisulfite, which means, that acetaldehyde is a rather powerful bisulfite binding agent.

The loosely bound SO_2 in waste liquors consists of a mixture of several bisulfite addition compounds of different stability. One part is more or less easily decomposed during the neutralization process; another part, however, is more resistant, and therefore the neutralized liquor always contains a certain amount of residual "loosely bound" SO_2 . The relative amounts of these two different fractions depend on the type of pulping. In rayon pulp waste liquors, where the pH is rather low (1-2) and only

relatively small amounts of SO_2 are present, the easily split fraction of loosely bound SO_2 is rapidly removed even by a short aeration of the waste liquor. The chalk added then only serves as a proper neutralizing agent. In liquors from base-rich strong pulp cookings, where the pH is about 3 and the content of loosely bound SO_2 is high, aeration has only slight effect and the decomposition of the bisulfite compounds proceeds at a slower rate on addition of chalk. This is illustrated by Figs. 77 and 78, showing

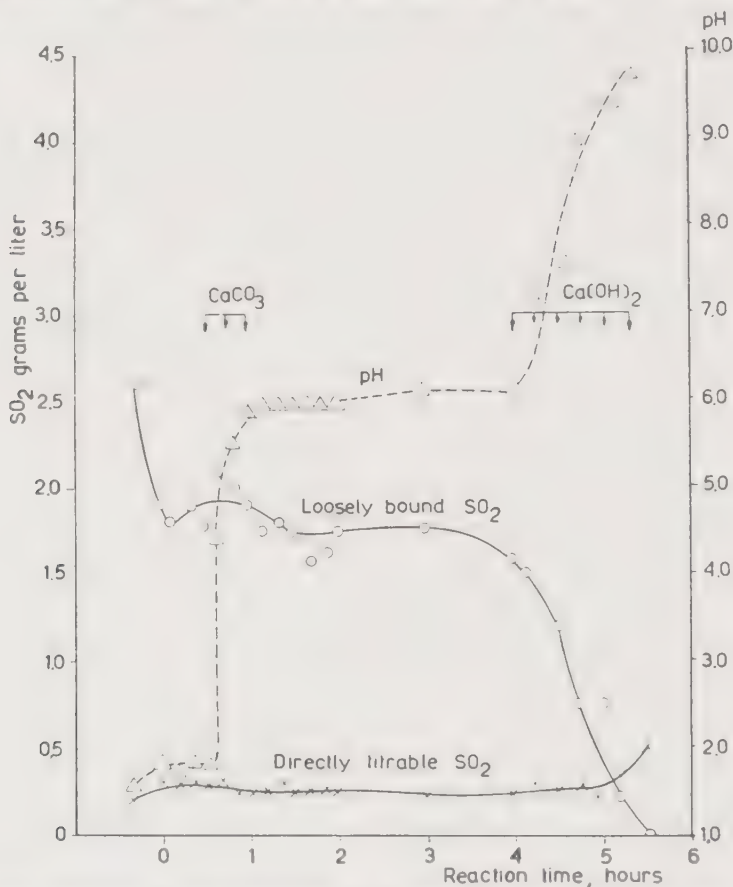


Fig. 77. Precipitation of "loosely bound" SO_2 from rayon pulp waste liquor by addition of CaCO_3 and Ca(OH)_2 at 90°C .

the changes in directly titrable and loosely bound SO_2 as well as in pH during the addition of calcium carbonate to a rayon pulp and a strong pulp waste liquor (37). In both cases a residue of about 1.75 g. loosely bound SO_2 per l. remains unaffected, when the pH of the liquors has reached the final value of about 6. As has been shown by E. Adler (38), these stable residues chiefly consist of formaldehyde and methylglyoxal bisulfite compounds. They may be split by raising the pH above 8, for example by the addition of calcium hydroxide; this is also shown in the Figs. 77 and 78.

The stable fraction of loosely bound SO_2 remaining in the neutralized liquor is not very harmful to fermentation. While sulfurous acid is rather toxic to commercial yeast, the yeast which has been used in sulfite alcohol fermentation, has acclimatized itself to those quantities of SO_2 which normally occur in neutralized waste liquors (159 a). In unpublished experiments performed in the author's institute by N. Mannbro, it has been found that the yield of ethanol can be increased by about 2%, if the

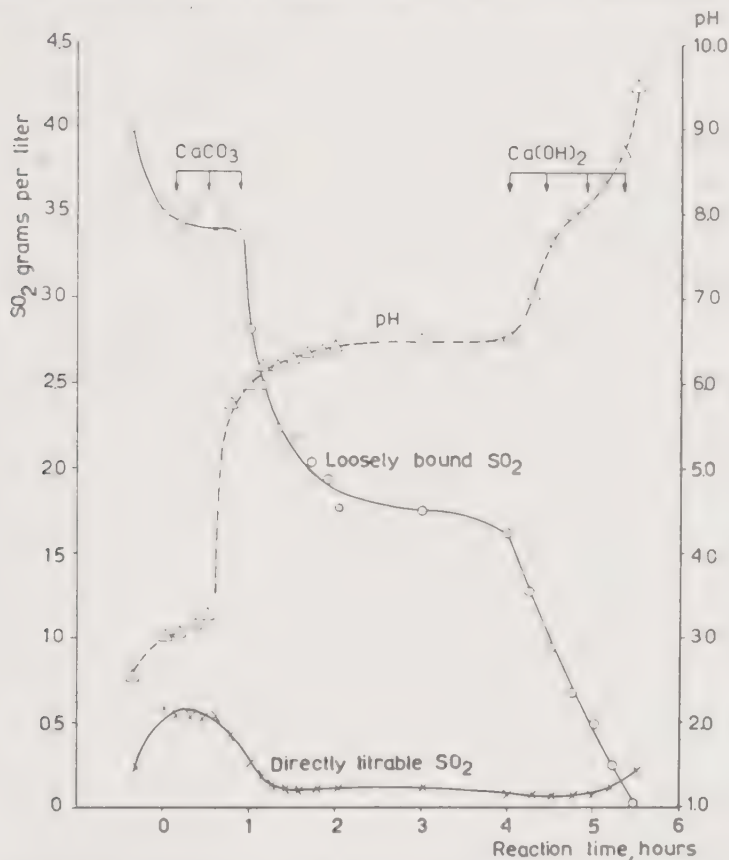


Fig. 78. Precipitation of "loosely bound" SO_2 from strong pulp waste liquor by addition of CaCO_3 and Ca(OH)_2 at 90°C .

loosely bound SO_2 is totally removed by making the waste liquor slightly alkaline and afterwards adjusting the pH to a value suitable for fermentation by adding a corresponding amount of unneutralized waste liquor.

Since the evaporation and burning of sulfite waste liquor has become an industrial process in Sweden (35), L. Enebo, E. Johnsson, and H. Lundin (159 b) have investigated the fermentation of concentrated waste liquors. They found that normal fermentation can be carried out with liquors containing up to 75 g. reducing substance per liter, i.e., 2-3 times the amount of reducing substance contained in the original waste liquors.

The ethyl alcohol produced from sulfite waste liquor contains more acetaldehyde than does alcohol obtained by fermentation of the agricultural products usually used in distilleries; this is doubtless caused by the residual amounts of loosely bound sulfurous acid present in the neutralized liquor.

Heating of the waste liquor with hydrochloric acid before neutralization results in complete removal of the loosely bound SO_2 , and subsequent fermentation will give a practically acetaldehyde-free ethanol (160). The same effect is obtained, if the sulfite waste liquor is made slightly alkaline for a short time prior to fermentation (cf. p. 461).

The crude spirit also contains about 3% of methyl alcohol, and usually a little fusel oil.

E. Hägglund and his co-workers (161) have investigated the origin of the methyl alcohol. By far the larger part of it is present in the waste liquor before the fermentation, but oddly enough, some methyl alcohol is also formed on fermentation of sugars containing methoxyl groups. This may be seen from the following figures on the sugar and methoxyl content of sulfite waste liquors before and after fermentation.

	Sugar g./l.	Methyl Alcohol g./l.
Waste liquor, not neutralized	25.3	1.24
Waste liquor, neutralized	24.1	1.14
Waste liquor, fermented	9.2	1.60
Waste liquor, distilled	8.9	0
Crude spirit		23.20

It was also found that fermentation of crystallized wood sugar, which contained 0.32% of methoxyl, caused all the methoxyl to be split off. The methoxyl could not be split off, however, under the conditions of sulfite pulping.

The impurities can be completely removed by rectification, so that "refined sulfite spirit" may be regarded as chemically pure.

The fusel oil was investigated more thoroughly by G. Komppa and Y. Talvitie (162), who found small amounts of furan and sylvan in it. Isobutyl and *n*-heptyl alcohols were also found. The chief constituents were amyl alcohol formed by fermentation, and *n*-hexyl alcohol. Limonene and camphene were shown to be present in the terpene fraction, and the terpene alcohols included large percentages of *l*-borneol and *d,l*-fenchyl alcohol. Guaiacol and azulene ($\text{C}_{15}\text{H}_{18}$) were present.

N. Hellström (163) gives the following composition for a sample of fusel oil which he investigated. The fractionation was carried out in a Podbielniak-Skärblom-Linder column.

	°
Water.....	17
Ethyl alcohol.....	12
Isobutyl alcohol.....	12
Isoamyl alcohol.....	35
Opt. act. amyl alcohol [$C_2H_5CH(CH_3)CH_2OH$].....	7
<i>n</i> -Hexyl alcohol.....	~ 2
Borneol.....	6
Guaiacol.....	~ 0.2
Esters.....	~ 1
Acids.....	~ 0.2
Undetermined.....	7.6

The fraction designated as "undetermined" may consist of a substance boiling above 160°C.

P. Klason and B. Segerfelt (164) had already found borneol, and B. Holmberg and E. Sunesson (165) found 14-22% of *l*-borneol in the crude material.

Borneol is formed during the cooking, as has already been mentioned. A. S. Wheeler and C. R. Harris (166) found that the crude oil from the relief gases contained 2% of borneol, of which 36% was *l*-borneol.

The sugars in sulfite waste liquor are also used for the preparation of bakers' yeast, fodder yeast, and even yeast for human nutrition (167). The first extensive investigations on this subject were made in Kymmene (Finland) by V. Krohn (168). Not only domestic yeasts, (*Saccharomyces cerevisiae*) but also wild ones like *Torula* and *Oidium* were used, and the remarkable statement was made that not only the hexoses but also the pentoses of the waste liquor were utilized by the last mentioned organisms.

The first experiments on the production of bakers' yeast were made by G. Heijkskjöld, N. R. Nilsson, and K. J. Klinga at the mill of Karskär in Sweden. On the basis of these experiments, the first bakers' yeast factory using sulfite waste liquor as a substrate was built at Björneborg in Finland and two plants later commenced operations in Canada.

H. Fink and R. Lechner (169), using *Torula* yeast, later succeeded in growing fodder yeast on sulfite waste liquor without the addition of any other source of nitrogen but ammonia. All of the fermentable sugars and the pentoses, as already had been shown by V. Krohn (168) were utilized. The practical working out of the problem was first accomplished by W. Claus at the Waldhof pulp mill in Germany. Detailed reports of the operations at this mill have been given by J. F. Saeman, E. Locke, and G. K. Dickerman (170) [cf. also W. H. Peterson, J. F. Snell, and W. C. Frazier (171)]. The yield of dry yeast was about 50% of the sugar, and the protein content of the yeast was 50-55%. Laboratory experiments concerning the growth of *torula* yeasts on sulfite waste liquor have recently also been described by R. D. Walker and R. A. Morgan (172).

Clostridium butylicum was shown by A. J. Wiley, M. J. Johnson, E. McCoy, and W. H. Peterson (173) to be most effective in fermenting sulfite waste liquors to acetone and butyl alcohol. It was found that 70-80% of the reducing substances could be fermented to a mixture containing 75% butyl alcohol, 20% acetone, and 5% ethyl alcohol.

Experiments concerning the production of lactic acid by fermentation of sulfite waste liquor have been reported by R. H. Leonard, W. H. Peterson, and M. J. Johnson (174). Waste liquor was treated with lime at pH 8.5, filtered, neutralized with carbon dioxide, and fermented with *Lactobacillus pentosus*. The fermented liquor was concentrated to 30% of the initial volume, acidified, and extracted with amyl alcohol or isophorone. The yield was 285 pounds of lactic acid and 75 pounds of acetic acid for each ton of pulp. If such a method were to be used on a large scale, new uses for lactic acid would be necessary.

According to the experiments of H. S. Daniels and J. L. McCarthy (174 a), about one half of the total initial reducing substances of a sulfite waste liquor could be converted into butyric acid on fermentation with *Clostridium polyfermenticum*.

The non-fermentable residues of the sulfite waste liquors are nearly always lost, except when they are concentrated by evaporation and burned. Previously this has not been profitable, since the heat of combustion did not even suffice for the concentration. Only more recently have procedures been advanced, particularly by C. Rosenblad and by T. Ramén (35) which give satisfactory results from the standpoint of heat balances (cf. p. 429).

Such uses would not even be considered if there were procedures for utilizing the liquors more profitably on a large scale.

Only minor amounts of sulfite waste liquors are used as road binders, as binders for coal briquettes, and as core binder in foundry practice. Adsorption charcoal can also be made from sulfite waste liquor. Its use as a dispersing agent in concrete has been proposed.

In this connection experiments on the use of lignin and lignin products as fertilizers and for soil improvement should also be mentioned. By pressure heating of lignosulfonates with ammonia, products containing 10-11% nitrogen were prepared, which showed fertilizer action (175). R. S. Aries (176) has reported investigations conducted under the auspices of the Northeastern Wood Utilization Council, which seem to be promising in several respects. Calcium lignosulfonate, applied at the rate of 10 tons per acre, increased the yield of shelled beans by 60%. Scholler-lignin increased the starch content of potatoes by 85%, but partially hydrolyzed wood gave less satisfactory results, as did sawdust.

Several other uses have been suggested for lignosulfonates or derivatives produced from them, e.g., as tanning agents, as ion exchangers, as emulsifying and dispersing agents, as protective colloids, as grinding aids, as reinforcing agents for rubber (177).

The tanning properties of lignosulfonic acid have been discussed by several authors (178). K. H. Gustavson (179) states that, although it is irreversibly adsorbed by the hide proteins, it cannot be considered as a proper tanning material. M. A. Buchanan, R. M. Lollar and D. D. Niemeyer (180) studied the influence of different woods and cooking conditions on the tanning properties of the sulfite waste liquors. None of the liquors examined were very satisfactory as they proved to be low affinity materials. Aspen liquor had the poorest tanning characteristics. In the spruce liquors the tanning properties seemed to run parallel with the content of the high-molecular fraction of lignosulfonic acids, which could be precipitated with β -naphthylamine. Thus, a rayon pulp liquor gave the best results. For high-grade tannings the lignosulfonates have to be used together with normal vegetable or synthetic tanning materials. Satisfactory tanning results with beech sulfite waste liquor have been reported by H. Zak (180a).

Chemical utilization of sulfite waste liquor often demands a separation of the lignin from the sugars. Such a process was introduced by G. C. Howard, who precipitated the lignosulfonic acid as a basic calcium salt (181). It has indeed been known for a long time that lignosulfonic acid can be precipitated from sulfite waste liquor by addition of lime, but the procedure of Howard is characterized by exact prescription of the amount of lime required. The liquor is first treated with enough lime to bring the pH to 10.5; this causes preferential precipitation of calcium sulfite which is returned to the factory to be used for the preparation of cooking acid. The separation is carried out in a Dorr separating vat. More lime is added to the remaining solution and the pH brought to 12. The basic calcium salt of lignosulfonic acid now settles out as a flocculent, yellow precipitate, from which the liquid is again separated by decantation. The precipitate is sucked dry on a filter, and further dried by pressing to a water content of 50%.

The mother liquor is treated with an excess of lime to remove a further fraction of lignin. This precipitate, together with the excess of lime, is used in the initial precipitation of the waste liquor.

After this three-stage treatment with lime, the waste liquor contains chiefly acid degradation products of sugars (lactic acid, saccharinic acids), which possess a low biochemical oxygen demand and may be released into the drains without doing any harm.

Experiments described by W. Lautsch (182) may be considered as a

new approach to the isolation of lignosulfonic acids from sulfite waste liquor. As has been mentioned in Chapter III (p. 260), W. Lautsch has prepared anion exchangers by condensation of alkali lignin with organic nitrogen bases. In contrast to hitherto known ion exchangers, these products were able to adsorb high-molecular substances, such as lignosulfonic acids. Metal ions were first removed from the waste liquors by a cation exchanger and the solution obtained was treated with an anion exchanger (condensation product of lignin with polyethyleneimine, ratio 9 : 1). Elution of the acids was accomplished by stepwise treatment with alkali. Eluates containing as much as 190 g. lignin per liter (calculated as ammonium lignosulfonate) could thus be obtained. The following figures from an experiment, in which the elution was accomplished with ammonia, may be instructive.

	Con- tent of Dry Sub- stance, g./l.	Lignin Content (as NH_4 - Ligno- sulfo- nate) g./l.	Elementary Composition of the NH_4 Salts					Elementary Composition Calcd. for N- and S-Free Lignin		
			C	H	OCH_3	S	N	C	H	OCH_3
Sulfite waste liq- uor, free from metal ions and mineral acids. .	70.6	59.0	50.3	5.63	9.88	7.90	3.43	—	—	—
First eluate.	98.2	97.0	52.47	6.12	11.96	7.65	3.21	66.60	6.46	15.27
Second eluate. . . .	126.3	125.6	52.08	5.79	12.05	7.44	3.60	66.44	5.92	15.28
Third eluate.	117.0	116.6	50.89	5.90	12.14	9.03	4.65	67.33	5.81	16.06

The basic calcium lignosulfonate obtained in the Howard process is used for the production of vanillin by heating under pressure with sodium hydroxide (cf. p. 229). About 4% of the lignin is obtained as vanillin, which is recovered in the form of the sodium salt by extraction with butanol. After removal of the butanol by distillation, the vanillin is purified via its bisulfite addition product (183).

The alkaline spent liquors from the vanillin process, containing desulfonated phenolic lignin degradation products, have been used for pulping comminuted wood wastes. At the end of this pulping process so much sugar acids have been formed that the alkali is used up and the lignin separates out on the pulp. A lignin-enriched pulp with 35-36% lignin is thus obtained, which has been used for the production of laminated sheets or as an extender for phenolic resins in molding compositions (184).

The lignin plastics obtained are slightly thermoplastic. Their water resistance is not quite satisfactory but is improved by the incorporation of phenolic resins.

In another vanillin process, developed by H. Hibbert and G. H. Tomlinson (185), sulfite waste liquor is concentrated and treated with sodium

hydroxide at an elevated temperature and pressure. The resultant solution is acidified with carbon dioxide and extracted with benzene. The vanillin is removed from the benzene solution by means of sodium bisulfite.

Rather good yields of vanillic acid in addition to vanillin, acetoguaiacone, and other substances, have been obtained by I. A. Pearl (186), who treated a lignosulfonate in alkaline solution with mercuric or silver oxide. Vanillic acid esters have proved themselves useful as food preservatives and disinfectants (187). Pearl (188) also found that 5-hydroxymercuri-vanillin is a good slime-control agent.

Not only the oxidative breakdown but also the reductive splitting offers possibilities of converting lignosulfonic acid into low-molecular organic chemicals. In this respect, pressure heating in alkaline solution and in the presence of alcohols as hydrogen donors appears to be of considerable interest (cf. Chapter III, p. 236). J. R. Salvesen, R. L. Hossfeld, and R. J. Lovin (189) reported that 32.6% catechols and 4.3% monohydric phenols were formed when lignosulfonate was heated with butyl alcohol and alkali for two hours at 270° C. R. Monnberg (190) heated a desulfonated product which he had prepared by heating sulfite waste liquor with lime at 160-170° C, with methanol and lime at 350° C, and obtained nearly 50% of phenolic and neutral products which were volatile under diminished pressure.

A. Björkman (191) has shown that the liquid products which are obtained on pressure heating of sulfite waste liquor with ethanol and alkali can be freed from sulfur by a subsequent hydrogenation over a sulfur-resistant catalyst.

For further information concerning the utilization of sulfite waste liquor the reader is referred to H. Vogel (192), I. A. Pearl (187), and H. F. Lewis (193) as well as to the extensive bibliography by C. J. West (191).

REFERENCES

1. Watt, C., and Burgess, H., U. S. Pat. 1,448, 1,449 (1854).
2. Tilghman, B. C., British Pat. 2,924 (1866); 385 (1867).
3. Cf. Kirchner, E., *Das Papier*, part III, Biberach, 1907, p. 15-27.
4. Pedersen, N., *Papier-Ztg.* **15**, 422, 787 (1890).
5. Lindsey, J. B., and Tollens, B., *Ann.* **267**, 341 (1892).
6. Klason, P., *Tek. Tid. Uppl. C. Kemi* **23**, 49 (1893).
7. Häggglund, E., Ekwall, A., and Hostomsky, J., *Acta Acad. Aboensis, Math. et Phys.* **6**, No. 15 (1932).
8. Häggglund, E., Johnson, T., and Busch, H., *Finnish Paper Timber J.* **16**, 282 (1934).
9. Häggglund, E., *Svensk Kem. Tid.* **37**, 120 (1925).
10. Häggglund, E., *Spensk Papperstidn.* **34**, 160 (1931); Häggglund, E., and Nihlén, H., *ibid.* **37**, 754 (1934).

11. Roe, R. B., *Ind. Eng. Chem.* **16**, 1808 (1924); *TAPPI Standards* T 202 m—45 (1945).
12. Hägglund, E., *Svensk Kem. Tid.* **43**, 115 (1931).
13. Martynov, M. F., *Chem. Abstr.* **33**, 7101 (1939).
14. Maass, O., Calhoun, J. M., and Yorston, F. H., *Can. J. Research* **5B**, 457 (1937); Maass, O., Calhoun, J. M., Yorston, F. H., and Cannon, J. J. R., *ibid.* **16B**, 242 (1938); **17B**, 121 (1939); also Du Rietz, C., and Kullgren, C., *Svensk Kem. Tid.* **42**, 179 (1930); **43**, 99, 161 (1931); **44**, 15 (1932); Du Rietz, C., *ibid.* **45**, 185 (1933); **46**, 136 (1934); **49**, 52 (1937).
15. Cf. Kullgren, C., *Svensk Papperstidn.* **36**, 14 (1933).
16. Goldfinger, G., *Paper Trade J.* **112**, No. 24, 29 (1941).
17. Escourrou, R., and Carpentier, P., *Paper Trade J.* **85**, No. 26, 37 (1927).
18. Hägglund, E., *Svensk Kem. Tid.* **38**, 181 (1926).
19. Hägglund, E., and Johansson, A., *Svensk Papperstidn.* **35**, 475 (1932).
20. Campbell, W. B., and Maass, O., *Can. J. Research* **2**, 42 (1930); cf. also Samuelson, S., and Haug, K., *Papir-J.* **19**, 218 (1931).
21. Birchard, W. H., *Paper Trade J.* **85**, No. 12, 59 (1927).
22. Hägglund, E., and Johnson, T., *Svensk Papperstidn.* **31**, 263 (1928); Hägglund, E., *ibid.* **32**, 84 (1929); **36**, 131 (1933).
23. Cf. also Klason, P., *Arkiv Kemi, Mineral. Geol.* **3**, No. 5 (1907); **4**, No. 1 (1910).
24. Hedlund, I., *Svensk Papperstidn.* **50**, No. 11B, (Jubilee Vol. E. Hägglund), 109 (1947); see also Hägglund, E., and Arnold, S., *Papier-Fabr.* **36**, 266 (1938).
- 24 a. Lange, P. W., *Svensk Papperstidn.* **50**, No. 11B, (Jubilee Vol. E. Hägglund), 130 (1947).
- 24 b. Bryde, O., *Norsk Skogindustri* **1**, 268 (1947).
25. Foerster, F., *Z. anorg. u. allgem. Chem.* **128**, 245 (1923).
26. Hägglund, E., Bäckström, C. H., Karanović, M., Runquist, L., and Vincent, O., *Svensk Papperstidn.* **38**, 659, 695 (1935).
27. Klason, P., *Arkiv Kemi, Mineral. Geol.* **4**, No. 1 (1910).
28. Cf. Wolkoff, L., *Zellstoff u. Papier* **5**, 355 (1925).
- 28 a. Stockman, L., *Svensk Papperstidn.* **54** (1951), in press.
29. Samuelson, O., and Westlin, A., *Svensk Papperstidn.* **50**, No. 11B, (Jubilee Vol. E. Hägglund), 149 (1947).
30. Groth, B., *Svensk Papperstidn.* **47**, 405 (1944).
31. Hägglund, E., *Svensk Papperstidn.* **49**, 191 (1946).
32. Eng, H., Österlöf, J., and Sillén, L. G., *Svensk Papperstidn.* **49**, 497 (1947).
33. Samuelson, O., and Öhgren, T., *Svensk Papperstidn.* **49**, 499 (1947).
34. Samuelson, O., *Svensk Papperstidn.* **49**, 575 (1947); Sillén, L. G., *ibid.* **50**, 339 (1947).
35. Ulfsparré, S., *Svensk Papperstidn.* **49**, 383 (1946); Brunes, B., Samuelson, O., and Ulfsparré, S., *Svensk Papperstidn.* **50**, No. 11B, (Jubilee Vol. E. Hägglund), 29 (1947); Nyman, O., *Svensk Papperstidn.* **49**, 73 (1946); Ramén, T., *ibid.* **49**, 418 (1946); Brauns, O., *ibid.* **44**, 216 (1941); **50**, No. 11B, 61 (1947); Rosenblad, C., *Northeastern Wood Utilization Council, New Haven, Bull.* No. **19**, 123 (1948).
36. Kerp, W., and Wöhler, P., *Arb. kaiserl. Gesundh.* **32**, 89 (1909).
37. Adler, E., *Svensk Papperstidn.* **50**, 261 (1947).
38. Adler, E., *Svensk Papperstidn.* **50**, No. 11B, (Jubilee Vol. E. Hägglund), 9 (1947).
39. Sundman, J., *Finnish Paper Timber J.* **29**, 52 (1947).
40. Samuelson, O., *Svensk Papperstidn.* **50**, 234 (1947).
41. Hägglund, E., and Boedeker, H., *Acta Acad. Aboensis, Math. et Phys.* **4**, No. 4 (1927).

42. Häggglund, E., and Larson, R., *Svensk Papperstidn.* **44**, 477 (1941).
43. Lindsey, B. J., and Tollens, B., *Ann.* **267**, 354 (1891); cf. also Krause, H., *Chem. Ind.* **39**, 217 (1906); Öman, E., *Tek. Tid. Uppl. C. Kemi* **45**, 104 (1915); Häggglund, E., *Acta Acad. Aboensis, Math. et Phys.* **3**, No. 3 (1923).
44. Häggglund, E., and Björkman, C. B., *Acta Acad. Aboensis, Math. et Phys.* **3**, No. 3 (1923).
45. Häggglund, E., *Ber.* **62**, 437 (1929).
46. Häggglund, E., *Ing. Vetenskaps Akad. Handl.* No. **86** (1928); *Ber.* **62**, 84 (1929); Häggglund, E., and Johnson, T., *Svensk Kem. Tid.* **41**, 8, 55 (1929); Häggglund, E., and Urban, H., *Ber.* **62**, 2046 (1929); cf. also Menzinsky, G., *Ber.* **63**, 822 (1935).
47. Häggglund, E., Johnson, T., and Urban, H., *Ber.* **63**, 1387 (1930).
48. Häggglund, E., and Nihlén, H., *Svensk Kem. Tid.* **47**, 141 (1935).
49. Dieckmann, R., *Technik und Praxis der Papierfabrikation*, II 1, Sulfitzellstoff, Berlin, 1923, p. 206.
50. Häggglund, E., *Papier-Fabr.* **26**, 657 (1938) (with Leino, E.).
- 50a. Häggglund, E., Stockman, L., and Löfström, P., *Svensk Papperstidn.* **53**, 551 (1950).
51. Heiwinkel, H., *Svensk Papperstidn.* **47**, 265 (1944).
52. Erdtman, H., *Svensk Papperstidn.* **45**, 374 (1942); Erdtman, H., Ericson, P., and Häggglund, E., *ibid.* **46**, 121 (1943); Samuelson, O., *ibid.* **46**, 583 (1943).
53. Adler, E., *Svensk Papperstidn.* **49**, 339 (1946).
54. Häggglund, E., Heiwinkel, H., and Bergek, T., *J. Prakt. Chem.* [2] **162**, 2 (1943); *Cellulosechemie* **21**, 108 (1943).
55. Häggglund, E., *Svensk Kem. Tid.* **36**, 284 (1924).
56. Häggglund, E., Johnson, T., and Trygg, L. H., *Svensk Papperstidn.* **32**, 815 (1929).
57. Samuelson, O., *Svensk Papperstidn.* **45**, 516 (1942).
58. Häggglund, E., and Nelson, B., *Svensk Papperstidn.* **47**, 226 (1944).
59. Pettersson, G., *Svensk Papperstidn.* **27**, 384 (1924).
60. Küng, A., *Svensk Papperstidn.* **49**, 145 (1946).
61. Klemm, P., *Handbuch der Papierkunde*, 3rd ed., Biberach, 1923, p. 250.
62. Klason, P., *Papier-Ztg.* **35**, 3781 (1910).
63. Richter, E., *Wochbl. Papierfabr.* **43**, 3485 (1912).
64. Cf. Lane, H. C., *Wochbl. Papierfabr.* **45**, 1858 (1914).
65. Roschier, H., *Finnish Paper Timber J.* **4**, 108 (1922).
66. Björkman, C. B., *Finnish Paper Timber J.* **9**, 45 (1927).
67. Tilghman, B. C., quoted by Kirchner, E., *Das Papier*, part III B and C, Biberach, 1907, p. 13.
68. Pictet, R. and Brélaz, G. L., German Pat. 26,331 (1883).
69. Cross, C. F., and Engelstad, A., *J. Soc. Chem. Ind. (London)* **43**, 253 T (1924); British Pat. 12,943 (1922); Chidester, G. H., and McGovern, J. N., *Paper Trade J.* **94**, No. 5, 40 (1932); Jonas, K. G., and Walter, P., *Wochbl. Papierfabr.* **62**, Special No., p. 55 (1931).
70. Cross, C. F., and Engelstad, A., *J. Soc. Chem. Ind. (London)* **43**, 253 T (1924).
71. Dorée, C., and Hall, L., *Cellulosechemie* **5**, 71 (1924).
72. Häggglund, E., and Johnson, T., *Svensk Papperstidn.* **31**, 263 (1928).
73. Tomlinson, G. H., and Wilcoxson, L. S., *Paper Trade J.* **110**, No. 15, 31 (1940); *Pulp Paper Mag. Can.* **41**, 391 (1940); Tomlinson, G. H., *ibid.* **45**, 817 (1944); Hatch, R. S., *Paper Trade J.* **122**, No. 11, 54 (1946).
74. Häggglund, E., *Svensk Kem. Tid.* **28**, 179 (1926); Häggglund, E., *ibid.* **33**, 115 (1931).

75. Aries, R. S., *Northeastern Wood Utilization Council, New Haven, Bull.* No. **7**, 65 (1945).
76. Hatch, R. S., *Pulp Paper Mag. Can.* **47**, No. 9, 80 (1946).
77. Johansson, D., *Svensk Papperstidn.* **33**, 916 (1930).
78. Hägglund, E., Sandelin, O., Nyman, C., Eriksson, T., Koskull, H. v., Ljungren, S., and Nihlén, H., *Svensk Papperstidn.* **37**, 133, 164, 196 (1934); **38**, 454 (1935); *Papier-Fabr.* **73**, 81 (1935).
79. Cf. Mühlsteh, W., *Cellulosechemie* **18**, 132 (1940).
80. Hägglund, E., *Iva* **1942**, No. 2.
81. Bray, M. W., and Curran, C. E., *Paper Trade J.* **105**, No. 20, 39 (1937); Chidester, G. H., McGovern, J. N., and McNaughton, G. C., *ibid.* **107**, No. 4, 32 (1938); Chidester, G. H., and McGovern, J. N., *ibid.* **107**, No. 13, 24 (1938); Chidester, G. H., Bray, M. W., and Curran, C. E., *ibid.* **109**, No. 13, 36 (1939); Curran, C. E., *ibid.* **103**, No. 11, 36 (1936); **106**, No. 23, 40 (1938).
82. Cf. Johansson, D., *Finnish Paper Timber J.* **21**, Special No. 54 (1939).
83. Kirchner, E., *Das Papier*, III B and C, Biberach, 1907. Zellstoff, Biberach, 1913, p. 153.
84. Schwalbe, C. G., *Papier-Fabr.* **24**, 38 (1926).
85. Hägglund, E., and Hansen, S., *Acta Acad. Aboensis, Math. et Phys.* **3**, No. 2 (1923).
86. Hägglund, E., *Cellulosechemie* **8**, 25 (1927); **9**, 38 (1928).
87. Schwalbe, C. G., and af Ekenstam, A., *Cellulosechemie* **10**, 1 (1929).
88. Cf., for example, Schmidt, E., *Papier-Fabr.* **36**, 565 (1938).
89. Hägglund, E., Holmberg, J., and Johnson, T., *Svensk Papperstidn.* Special No. Sept. 7-8 (1936), p. 37.
90. Erdtman, H., *Ann.* **539**, 116 (1939).
91. Koch, J. E., and Krieg, W., *Chem.-Ztg.* **15**, 140 (1938).
92. Hägglund, E., and Johnson, T., *Z. angew. Chem.* **40**, 1101 (1927).
93. Erdtman, H., *Svensk Papperstidn.* **46**, 226 (1943).
94. Erdtman, H., *Svensk Papperstidn.* **43**, 255 (1940); *Tappi* **32**, 303 (1949).
95. Graham, J. A., British Pat. 5,365 (1882).
96. Haglund, G., *Svensk Pappersmasse Tid.* **1934**, 124; Bradley, L., and McKeefe, E., German Pat. 375,053 (1923).
97. Lindgren, B. O., *Acta Chem. Scand.* **1**, 799 (1947); **3**, 1011 (1949).
- 97 a. Pew, J. C., *Tappi* **32**, 39 (1949).
98. Hägglund, E., and Hedborg, F., *Svensk Papperstidn.* **38**, 318 (1935).
99. Hägglund, E., and Larsson, S., *Svensk Papperstidn.* **40**, 356 (1937).
100. Erdtman, H., *Svensk Papperstidn.* **43**, 241 (1940).
101. Trendelenburg, R., *Das Holz als Rohstoff*, Munich and Berlin, 1939, p. 134 ff.
102. Jayme, G., and Lochmüller-Kerler, E., *Holz Roh- u. Werkstoff* **6**, 274 (1943).
103. Hägglund, E., Améen, W., Bergek, T., Lindholm, I., and Nihlén, H., *Svenska Skogsvårdsför. Tid.* **1940**, 105.
104. Richter, G. A., *Ind. Eng. Chem.* **33**, 532, 1518 (1941).
105. Bray, M. W., *Paper Trade J.* **120**, No. 21, 44 (1945).
- 105 a. Lautsch, W., *Cellulosechemie* **21**, 51 (1943).
106. Cf. Richter, G. A., *Ind. Eng. Chem.* **33**, 532 (1941).
107. Hägglund, E., *Papier-Fabr.* **34**, 313 (1936).
108. Hägglund, E., *Svensk Papperstidn.* **41**, 194 (1938).
109. Green, H., and Yorston, F. H., *Pulp Paper Mag. Can.* **40**, 244 (1939).
110. Anderson, C. A., *Pulp Paper Mag. Can.* **47**, No. 1, 43 (1946).

111. Bildt, O., *Svensk Papperstidn.* **41**, 261 (1938).
112. Jayme, G., and Grøgaard, L., *Cellulosechemie* **18**, 34, 42 (1940); *Papier-Fabr.* **38**, 93, 101, 113 (1940).
113. Jayme, G., and Harders-Steinhäuser, M., *Holzforschung* **1**, 33 (1947); Grøgaard, L., *Svensk Papperstidn.* **49**, 271 (1946).
114. Freudenberg, K., and Dürr, W.; cf. Klein, G., *Handbuch der Pflanzenanalyse*, vol. 3, part 2, Wien, 1932, p. 155.
115. Jayme, G., and Wettstein, R., *Papier-Fabr.* **36**, 519 (1938); Jayme, G., and Hanke, G., *Cellulosechemie* **21**, 127 (1943).
116. Dolmetsch, H., Franz, E., and Correns, E., *Kolloid-Z.* **106**, 174 (1944).
117. Jayme, G., and Lochmüller-Kerler, E., *Holz Roh- u. Werkstoff* **5**, 10, 377 (1942).
118. Jayme, G., and Rothamel, L., *Papier-Fabr.* **40**, 26, 34, 44 (1942).
119. Staudinger, H., *Jentgen's Kunstseide u. Zellwolle* **24**, 511 (1942).
120. Staudinger, H., *Papier-Fabr.* **36**, 473 (1938).
121. Dolmetsch, H., and Reinecke, F., *Zellwolle u. Deut. Kunstseiden Ztg.* **5**, 299, (1939); *Chem. Zentr.* **1940**, **I**, 154.
122. Staudinger, H., and Sorkin, M., *Ber.* **70**, 1565 (1937).
123. Cf., for example, Tydén, H., Dissertation, Stockholm, 1942.
124. Staudinger, H., and Reinecke, F., *Papier-Fabr.* **36**, 489 (1938).
125. Staudinger, H., and Dreher, E., *Ber.* **69**, 1091 (1936).
126. Wurz, O., and Swoboda, O., *Papier-Fabr.* **40**, 22 (1942).
127. Wurz, O., and Swoboda, O., *Svensk Papperstidn.* **50**, 26 (1947).
128. Wulsch, F., *Papier-Fabr.* **40**, 161 (1942).
129. Heuser, E., and Samuelsen, S., *Papier-Fabr.* **20**, 1249, 1285, 1321 (1922).
130. Aschan, O., *Teknikern* (Helsingfors) **33**, 73 (1923).
131. Wahlberg, H. E., *Svensk Papperstidn.* **25**, 401 (1922).
132. Öman, E., *Svensk Papperstidn.* **27**, 444, 466 (1924).
133. Hägglund, E., and Hedman, E. O., *Svensk Papperstidn.* **28**, 183 (1925).
134. Schwartz, H., McCarthy, J. L., and Hibbert, H., *Paper Trade J.* **111**, No. 18, 33 (1940).
- 134 a. Adler, E., and Häggroth, S., *Svensk Papperstidn.* **53**, 321 (1950).
135. Kullgren, C., *Svensk Kem. Tid.* **53**, 99 (1931).
136. Hägglund, E., Fehrm, B., and Waenerlund, L., *Svensk Papperstidn.* **49**, 202 (1946).
- 136 a. Adler, E., and Häggroth, S., *Svensk Papperstidn.* **53**, 287 (1950).
- 136 b. Lewis, S. J., *J. Soc. Dyer Colourists* **34**, 167 (1918); **37**, 201 (1921); **38**, 76, 99 (1922); **40**, 29, 111 (1924); Kirmreuther, H., *Papier-Fabr.* **24**, 106 (1926); Hägglund, E., and Johnson, T., *Z. angew. Chem.* **40**, 1101 (1927).
- 136 c. Adler, E., and Häggroth, S., unpublished results.
137. Cross, W. E., *Ber.* **43**, 1526 (1910).
138. Hönig, M., *Chem.-Ztg.* **36**, 889 (1912).
139. Hägglund, E., *Holzchemie*, 1st ed., Leipzig, 1928, p. 209.
140. Jonas, K. G., *Wochbl. Papierfabr.* **56**, Special No. 24A, 85 (1925).
141. Schwalbe, C. G., and Becker, E., *Z. angew. Chem.* **32**, 231 (1919).
142. Giller, O., cf. abstract by Krüger, A., *Finnish Paper Timber J.* **17**, 58 (1935); Hodakoff, K. V., and Kallistratoff, G. A., cf. abstract by Krüger, A., *Finnish Paper Timber J.* **17**, 58 (1935).
143. Routala, O., and Yli-Jama, O., *Finnish Paper Timber J.* **18**, 350 (1936); Routala, O., and Vauhkonen, T., *Chem. Zentr.* **1937**, **I**, 1055; **1938**, **I**, 475.

144. Bergström, H., *Papier-Fabr.* **7**, 1314 (1909); **8**, 506 (1910); **10**, 677 (1912).
145. Häggglund, E., Die Sulfitablauge und ihre Verarbeitung auf Alkohol, Braun-schweig, 1921, p. 51. For recent investigations, cf. Häggglund, E., *Svensk Papperstidn.* **46**, 143 (1943).
146. Klason, P., *Ber.* **33**, 2343 (1900).
147. Schorger, A. W., *Ind. Eng. Chem.* **10**, 258 (1918).
148. Aschan, O., Naftenföreningar, etc., Helsingfors, 1926, p. 338.
149. Örtenblad, T., *Tek. Tid. Uppl. C. Kemi* **48**, 108 (1918); Holtan, E., *Papir-J.* **29**, 151 (1941); Waller, A., *Svensk Papperstidn.* **44**, 427 (1941).
150. Kertész, Z., *Chem.-Ztg.* **40**, 945 (1916).
151. Boedtker, E., *J. pharm. chim.* [8] **9**, 417 (1929).
152. Routala, O., and Pohjola, A., *Finnish Paper Timber J.* **16**, 289 (1934). For purification of the crude cymene cf. also Schorger, A. W., *J. Am. Chem. Soc.* **39**, 2671 (1917); Wheeler, A. S., and Smithey, I. W., *ibid.* **43**, 2611 (1921); Austerweil, G., and Lemay, L., *Bull. soc. chim. France* **41**, 454 (1927); Karvonen, A., *Ber.* **56**, 1824 (1923); Mann, C. H., Montonna, R. E., and Larian, M. G., *Ind. Eng. Chem.* **28**, 598 (1936).
153. Wienhaus, H., *Papier-Fabr.* **35**, 385 (1937).
154. Anon., *Chem. Industries* **53**, 844 (1943); *Pulp & Paper Ind.* **19**, No. 6, 18 (1945).
155. Ekström, G., *Svensk Trävaru-Tidn.* **58**, 256 (1942); Sankey, C. A., and Rosten, M. M., *Pulp Paper Mag. Canada* **45**, No. 3, 171, 188 (1944).
156. Cf., for example, Nihlén, H., *Svensk Papperstidn.* **42**, 593 (1939).
157. Bergson, C. R., *Svensk Papperstidn.* **43**, 2 (1940).
158. Johansson, D., *Svensk Papperstidn.* **43**, 36 (1940).
159. Johansson, D., *Svensk Papperstidn.* **42**, 582 (1939).
- 159 a. Gadd, G. O., *Finnish Paper Timber J.* **28**, No. 7A, 61 (1946).
- 159 b. Enebo, L., Johnsson, E., and Lundin, H., *Svensk Papperstidn.* **50**, No. 11B (Jubilee Vol. E. Häggglund), 72 (1947).
160. Häggglund, E., and Sundroos, B. E., *Acta Acad. Aboensis, Math. et Phys.* **2**, No. 6, 16 (1923).
161. Häggglund, E., *Svensk Papperstidn.* **47**, 230 (1944).
162. Komppa, G., and Talvitie, Y., *Chem. Zentr.* **1931**, II, 2074.
163. Hellström, N., *Svensk Kem. Tid.* **55**, 161 (1943).
164. Klason, P., and Segerfelt, B., *Svensk Kem. Tid.* **23**, 149 (1911); *Arkiv Kemi, Mineral. Geol.* **4**, No. 20 (1913).
165. Holmberg, B., and Sunesson, E., *Svensk Kem. Tid.* **35**, 215 (1923).
166. Wheeler, A. S., and Harris, C. R., *J. Am. Chem. Soc.* **47**, 2836 (1925).
167. Cf. Häggglund, E., *Papier-Fabr.* **28**, 643, 707 (1930).
168. Krohn, V., *Ann. Acad. Sci. Fennicae* **A23**, No. 8 (1924).
169. Fink, H., and Lechner, R., *Angew. Chem.* **49**, 775 (1936).
170. Saeman, J. F., Locke, E. G., and Dickerman, G. K., *Paper Trade J.* **123**, No. 12, 38 (1946); cf. also *Northeastern Wood Utilization Council, New Haven, Bull.* No. 12 (1946).
171. Peterson, W. H., Snell, J. F., and Frazier, W. C., *Ind. Eng. Chem.* **37**, 30 (1945).
172. Walker, R. D., and Morgan, R. A., *Paper Trade J.* **123**, No. 6, 43 (1946).
173. Wiley, A. J., McCoy, E., Johnson, M. J., and Peterson, W. H., *Ind. Eng. Chem.* **33**, 606 (1941).
174. Leonard, R. H., Peterson, W. H., and Johnson, M. J., *Ind. Eng. Chem.* **40**, 57 (1948).

- 174 a. Daniels, H. S., and McCarthy, J. L., *Techn. Assoc. Pap.* **31**, 626 (1948).
175. Kobe, K. A., Layman, I. H., and Armbruster, F. R., *Ind. Eng. Chem.* **28**, 571 (1936); Phillips, M., Goss, M. I., Brown, B. E., and Reid, F. R., *Wash. Acad. Sci.* **24**, 1 (1934); *J. Agr. Research.* **53**, 209 (1936).
176. Aries, R. S., *Paper Trade J.* **123**, No. 21, 47 (1946); cf. also Aries, R. S., *North-eastern Wood Utilization Council, New Haven, Bull.* No. **7**, 65 (1945).
177. Howard, G. C., *Chem. Industries* **48**, 724 (1941).
178. Johnson, A. M., and Marshall, H. B., *Pulp Paper Mag. Can.* **50**, No. 8, 98 (1949).
179. Gustavson, K. H., *Svensk Papperstidn.* **45**, 193 (1942); *Tek. Tid. Kemi* **73**, 59 (1943); *Ing. Vetenskapsakad. Handl.* No. **177** (1944); Gustavson, K. H., and Larsson, A., *Svensk Papperstidn.* **50**, No. 11B (Jubilee Vol. E. Hagglund), 101 (1947); Gustavson, K. H., and Tomlinson, J., *J. Soc. Leather Trades' Chemists* **32**, 165 (1948); Gustavson, K. H., *Svensk Kem. Tid.* **60**, 200 (1948).
180. Buchanan, M. A., Lollar, R. M., and Niemeyer, D. D., *Paper Trade J.* **124**, No. 18, 38 (1947).
- 180 a. Zak, H., *Österreich. Papier-Ztg.* **56**, No. 3, 5 (1950).
181. Howard, G. C., U. S. Pat. 1,699,845 (1929); 1,856,558 (1932).
182. Lautsch, W., *Die Chemie* **57**, 149 (1944).
183. U. S. Pat. 2,104,701 (1938).
184. Howard, G. C., *Modern Plastics* **17**, No. 3, 96 (1939); Meiler, J. G., *Modern Plastics* **20**, No. 1, 64 (1942).
185. Hibbert, H., and Tomlinson, G. H., Jr., U. S. Pat. 2,069,185 (1935).
186. Pearl, I. A., *J. Am. Chem. Soc.* **71**, 2196 (1949).
187. Pearl, I. A., *Chem. Eng. News* **26**, 2950 (1948); *Tappi* **33**, 263 (1950).
188. Pearl, I. A., *J. Am. Chem. Soc.* **70**, 2008 (1948).
189. Salvesen, J. R., Hossfeld, R. L., and Lovin, R. J., U. S. Pats. 2,405,450 and 2,405,451 (1946).
190. Monnberg, R., *Finnish Paper Timber J.* **31**, No. 7A, 11 (1949).
191. Björkman, A., *Transactions Royal Inst. Technology, Stockholm*, No. 31 (1950).
192. Vogel, H., *Sulfitzellstoff-Ablaugen*, Basel, 1948.
193. Lewis, H. F., *Tech. Assoc. Papers* **31**, 448 (1948).
194. West, C. J., *Bibliography of Pulp and Paper Manufacture 1936-1945*, New York, 1947, and following volumes.

CHAPTER VI

THE PULPING OF WOOD BY AQUEOUS ALKALIES

I. History of the Alkaline Pulping Process

The isolation of plant fibers by means of aqueous alkalies has been known for a long time. The present method of making alkali pulp, however, was introduced only in the middle of the last century, by C. Watt and H. Burgess (1). In this method the wood was for the first time cooked with alkali under pressure.

The first mill was built in the United States in 1860. Six years later a plant patterned after this one was constructed in England, and after six more years, alkali pulp production was begun simultaneously in Germany and Sweden.

For a long time this procedure involved great technical difficulties, especially in the cooking process. In this connection one should mention the process of A. Ungerer, in which the digestion was carried out in a sort of diffusion battery employing a counter-current method (2). Not only the cooking, but also the alkali recovery, so necessary for economic practicability, presented difficulties.

C. F. Dahl (2) found, more or less by chance, that it was expedient to replace the lost alkali with sodium sulfate rather than with soda. This sulfate was reduced to sodium sulfide when the organic matter was burned for the purpose of recovering the alkali. Reuse of the recovered alkali yielded a cooking liquor more or less rich in sodium sulfide, which improved the yield and quality of the pulp (from conifers). This improvement constituted the beginning of the so-called *sulfate process*, which is now responsible for the production of by far the largest portion of the world's alkali pulp. Cooking with sulfur-free sodium hydroxyde solution is called the *soda process*, as the losses of alkali are replaced by addition of soda to the black liquor. The use of the soda process is by now practically limited to the pulping of deciduous woods. Unpleasant odors were, to be sure, a disadvantage of the sulfate process. However, the introduction of the Tomlinson oven, and the thorough cleansing of waste gases, in practice, solved the problem of the complete elimination of evil-smelling compounds. These consist mainly of methyl mercaptan, and are

formed in small quantities during the cooking of the pulp and the regeneration of the alkali (cf. p. 490).

The alkali pulp process was for a long time more expensive than the sulfite method, but had, nevertheless, the advantage that nearly all woods could be used, including pine and especially saw mill waste which were out of the question for the sulfite process. The sulfate process has experienced a tremendous development because of the recent increase in emphasis on packaging, for which "sulfate kraft paper" has proved exceptionally suitable, and because of rationalization of the operation and economies made possible chiefly by increasing the capacity of the plants. The development of the sulfate process has been further stimulated by the fact that it has become possible, by the use of suitable bleaching processes, to bleach sulfate kraft pulp of relatively high lignin content to whiteness without impairing the strength of the fibers. Because of these facts, the sulfate method has already come into competition with the sulfite process, and will do so still more in the future. This competition has occurred in still another market for sulfate pulp, namely that of cellulose for rayon. R. E. Dörr (3) and his co-workers, by combining an acid pre-hydrolysis with a terminal sulfate cooking, have succeeded in preparing from wood a pulp which is excellent for textile rayon silk and cord. The alkali procedure here permits the use of resinous woods such as pine.

The extraordinarily rapid development of this field is clearly illustrated by the following figures for the world production of sulfate pulp:

Year	Tons
1914	403,000
1924	946,000
1929	2,041,000
1935	3,018,000
1938	4,240,000
1950	about 8,000,000

II. The Chemistry of the Alkaline Pulping Processes

A. MAIN COMPONENTS OF THE BLACK LIQUOR

The first investigations in this field were made by P. Klason (4), who analyzed the black liquor obtained in the soda process.

His results indicated, that the waste liquor contained appreciable quantities of hydroxy acids and lactones.

In an investigation of the alkaline pulping of spruce, E. Hägglund (5) obtained the following yields (6):

Per Cent of the Weight of the Wood

Cellulose	42.8
Alkali lignin	21.6
Resin, fats, etc.	2.2
Lactones and hydroxy (saccharinic, lactic) acids	18.2
Acetic acid	3.2
Formic acid	1.7
Methyl alcohol	0.4
Lignin soluble in acid solution	6.9

The cooking had evidently proceeded very far, since the yield of cellulose was so small.

B. ALKALI CONSUMPTION AND REACTION VELOCITY IN COOKS WITH CAUSTIC SODA

The question of the alkali-consumption during the cooking was formerly very much discussed (7, 8). The variations in consumption are obviously connected with the degree of cooking.

In actual practice, about 18 kg. of "active" alkali per 100 kg. of wood are used for the preparation, from pine wood, of kraft pulps with a Roe number of 6-8. If, however, larger quantities of alkali are added at the beginning of the cooking, the NaOH consumption increases markedly (9).

F. E. Brauns and W. S. Grimes (10) found an alkali consumption of 16% in the cooking of American spruce wood with caustic soda. They attempted to determine its distribution. Of the total 16%, 1.5% was consumed by the acetic and formic acids formed, 3-4% by the lignin, and the remaining 10.5-11.5% chiefly by the dissolved carbohydrates (hydroxy acids) but also by adsorption by the remaining pulp.

A number of investigations on the speed of the digestion of wood by caustic soda have also been made over the years (11, 12).

The question as to whether the reaction velocity corresponds to any formula has also been considered. S. Arrhenius was the first to carry out such a calculation, basing his work on the experiments of J. Bruun. He finally decided that the reaction velocity obeyed the laws of a uni-molecular reaction. The temperature dependence could also be calculated, with some degree of accuracy, from the well-known formula:

$$q_1 = q_0 e^{A(T_1 - T_0)/T_1 T_0}$$

Here q_0 and q_1 are the reaction rate constants at the absolute temperatures T_0 and T_1 .

Later investigations by S. Schmidt-Nielsen and T. Overwien showed

that the "constants" of the monomolecular reaction had so marked a drift that by the end of the cooking they were only one third to one fifth as large as at the beginning.

G. L. Larocque and O. Maass believed that they had proved the dissolution with alkali to be a monomolecular reaction. The sole exception was the last 2% of lignin, which was thought to be bound in a different way.

If one uses as a basis the figures of E. Hägglund and R. Hedlund (12) for the release of lignin on cooking spruce, and at the same time makes allowance for the time required to heat to cooking temperature, the following "constants" can be calculated for a monomolecular reaction: They also show an appreciable drift.

Cooking Time in hrs. After Reaching 150°C	Lignin in Residue g./100 g. Wood	$K \times 100$	Cooking Time in hrs. After Reaching 160°C	Lignin in Residue g./100 g. Wood	$K \times 100$	Cooking Time in hrs. After Reaching 170°C	Lignin in Residue g./100 g. Wood	$K \times 100$
0	25.4	—	0	23.9	—	0	23.0	—
1.5	22.9	0.159	1.0	18.4	0.435	1.0	12.6	1.000
4.5	17.1	0.146	2.0	15.3	0.372	1.5	10.0	0.924
8.0	14.4	0.118	3.0	12.3	0.372	2.0	7.86	0.893
10.5	12.3	0.115	4.0	10.04	0.362	2.5	6.04	0.890
13.0	10.8	0.110	5.0	8.15	0.358	3.0	4.77	0.874
15.5	8.83	0.114	6.0	7.06	0.339	3.5	4.17	0.812
18.5	8.22	0.102	7.0	5.65	0.344	4.0	3.46	0.789
19.5	7.47	0.105	8.0	5.03	0.326	4.5	3.21	0.721
21.0	7.23	0.100	—	—	—	5.0	2.89	0.692

The values of K show that it is not possible by these methods to determine for certain whether the reaction proceeds monomolecularly. It should be mentioned, however, that the rate of diffusion of the lignin would affect the rate of dissolution.

The question of the change in alkalinity during an alkali digestion was investigated by, among others, C. Christiansen (8) and even more fully by C. Kullgren (13). The latter measured the hydroxyl ion concentration by the method of K. Koelichen (13 a), in which the rate of decomposition of diacetone alcohol in acetone is proportional to the OH^- concentration. The results are related under heading C.

C. THE EFFECT OF THE SULFIDITY IN SULFATE COOKS

1. Rate of Delignification and Pulp Strength. Numerous experiments have been conducted on the digestion of wood with solutions of sodium sulfide alone, or with mixtures of sodium sulfide and sodium hydroxide, so-called "sulfate liquor." The results were compared with those obtained with pure sodium hydroxide.

S. Arrhenius (14) found, on the basis of experiments by J. Bruun, that

sodium hydroxide and sodium sulfide in equivalent concentrations have equally strong dissolving actions. Sulfide liquors attack cellulose less. In this respect a sulfate liquor containing 16% of Na_2S (in terms of total effective alkalis), is even better.

E. Hägglund and R. Hedlund (12) made a study of the effect of the sulfide content of the cooking liquor. Fig. 79 shows the dissolution of lignin from spruce wood at 160°C at various sulfidities. The sulfidity (in %) is given by the expression

$$100 \times \frac{\text{g. Na}_2\text{S (as NaOH)}}{\text{g. NaOH} + \text{g. Na}_2\text{S (as NaOH)}}$$

The rate of dissolution of lignin increased with increased sulfide content of the liquor. The last residue of the lignin dissolves very slowly. With

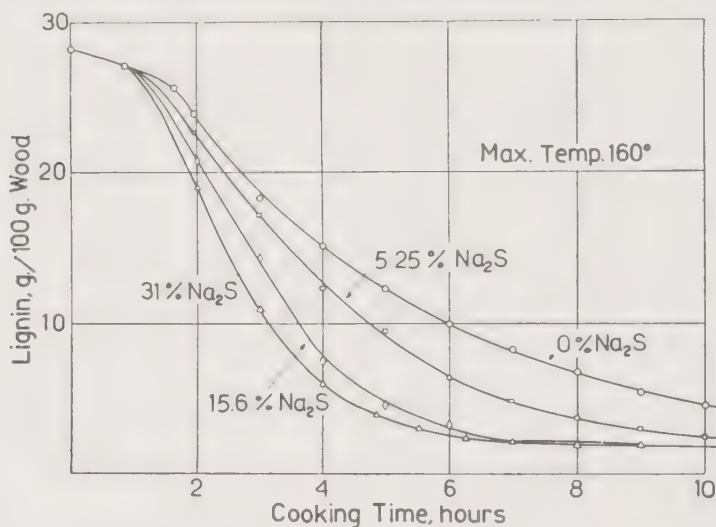


Fig. 79. Dissolution of lignin from spruce wood at 160°C . Active alkali ($\text{NaOH} + \text{Na}_2\text{S}$), expressed as NaOH , 24.2% of the dry wood.

sulfur-free alkaline liquor it is very difficult to obtain a pulp with a lignin content lower than about 10% from spruce wood. The cooking time of pulp with the same degree of delignification (Roe number) can be considerably reduced by increasing the sulfide content of the white liquor. This is illustrated in Fig. 80, which also shows the results of runs made at different maximum temperatures. In order to obtain a Roe Number of 5, one must, for example, at 160°C , cook only $6\frac{1}{2}$ hours with 40% sulfidity in contrast to $9\frac{1}{2}$ hours with 12% sulfidity. It can thus be seen that an increase in sulfidity decreases the cooking time necessary to reach a predetermined degree of delignification. How this affects the properties of the pulp is presented in Fig. 81, which shows the tensile strength after cooking

at a maximum temperature of 160°C. It is obvious, that the strength is decreased by decreasing the sulfidity. Very similar curves are obtained for the burst and tear strengths (22).

Kullgren (13) found that, in cooks with sulfur-free alkaline liquor, the dissolving action of the caustic soda decreases greatly between 130°C and

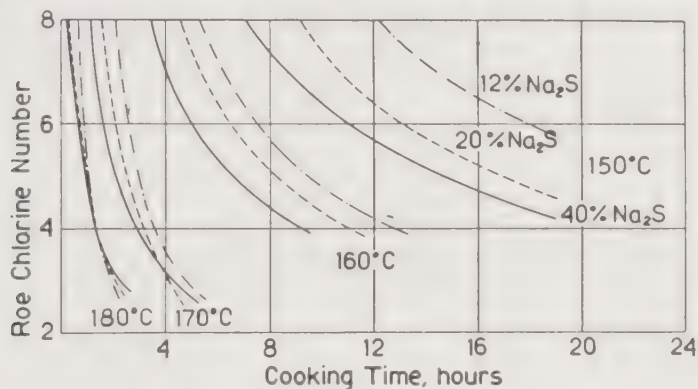


Fig. 80. Sulfate cooks on pine wood. Active alkali 22% of the dry wood.

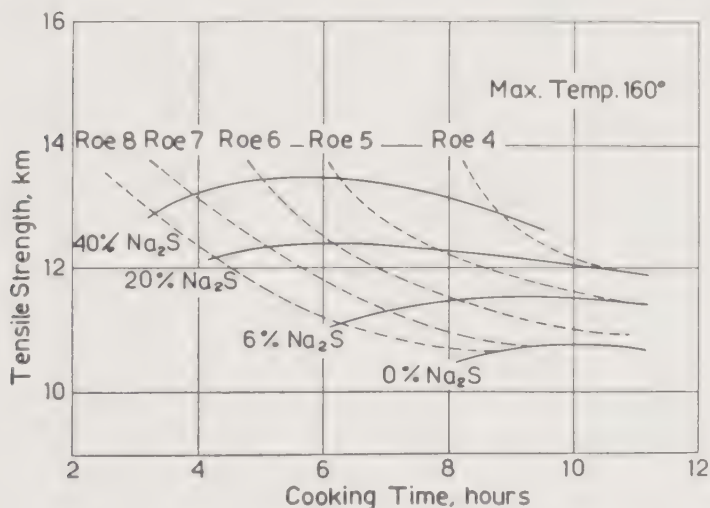


Fig. 81. Sulfate cooks on pine wood. Active alkali 22% of the dry wood.

150°C, but that above 160°C the rate of dissolution increases again. In the case of the sulfate liquors, this decrease in activity was negligible. These results are in good accordance with the findings from the author's laboratory (16), which are based on sulfate and pure sodium hydroxide cooks on spruce wood at 130°C and 140°C. Fig. 82 shows that the amount of carbohydrate dissolved is almost exactly the same in both types of cooks. The dissolution of lignin in the sulfate cook proceeds relatively unhindered with only a small decrease in the reaction rate during the entire cooking

time, while the pure alkali cook shows, at first, a rapid dissolution of lignin, the same as in the sulfate cook, but then a rapid decrease in rate of reaction after about a third of the lignin has been dissolved.

The favorable effect of sodium sulfide in the sulfate cooking process has been interpreted in many different ways. Thus, it has been believed that the sulfide was oxidized to sulfate by the oxygen occurring in the

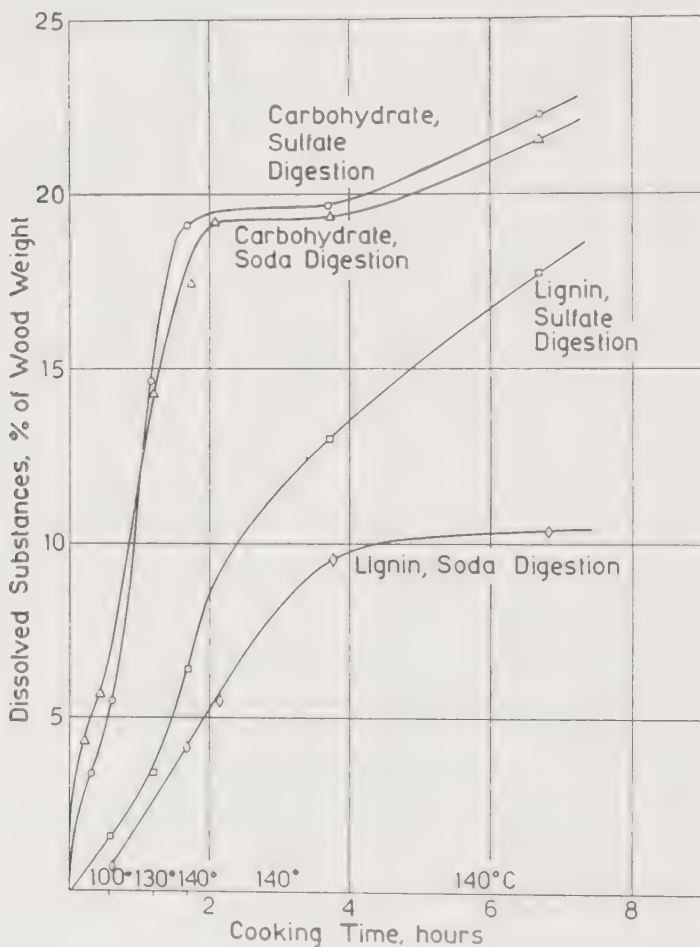


Fig. 82. Dissolution¹ of carbohydrates and lignin in soda and sulfate cooks at 140°C. Sulfidity 30%. Active alkali 25% of the dry wood.

organic constituents of the wood or of the liquor. The opinion has also been advanced, that the sulfide acts more or less only as a catalyst (17). E. Hägglund (9), however, in agreement with the results of P. Klason (18) and C. Kullgren (15), found that the sulfide content of the cooking liquor decreased gradually during the cooking to half its original value [cf. also (18 a)].

P. Klason and B. Segerfelt (19) made the important observation that

the lignin in the black liquor contains organically bound sulfur. They gave the following figures for the distribution of the sulfur in the black liquor at the end of the cooking:

	%
Bound to lignin.....	36.7
Bound to other organic substances of the black liquor	15.1
Contained in volatile organic substances.....	15.0
As sodium sulfide.....	16.8
Undetermined	16.4
	<hr/> 100.0

The composition of the black liquors resulting from the sulfate and soda processes are, according to Klason, approximately the same, except for the different composition of the lignin.

O. Anderzén and B. Holmberg (20) analyzed the alkali lignin, which precipitated from black liquor on acidification, and found that it contained 2.5% sulfur.

The supposition has been expressed that as the sulfur is combined with the lignin, the sodium sulfide only gradually becomes active as sodium hydroxide. Klason regarded this to be the explanation of the protective action of the sulfide. This, however, can not be correct since, in the beginning of a sulfate cook there is always a considerable surplus of sodium hydroxide present, whereas at the end of the cook, when the concentration of the hydroxide is low, the sodium sulfide is nearly completely hydrolyzed into sodium hydroxide and sodium hydrosulfide. C. Kullgren (15) is of the opinion that this hydrolysis is almost complete from the beginning, whereas G. Martin (15a) recently estimated that about 40% of the sulfide is hydrolyzed at the beginning, and about 90% at the end of a typical sulfate cook.

C. Kullgren presumes (15) that in that part of the cooking during which the maximum temperature is maintained, the hydroxyl ion concentration of the sulfate liquor decreases faster than that of the caustic soda liquor. The sodium hydrosulfide might by its action produce sulfur-containing compounds which would use up sodium hydroxide, and so decrease the hydroxyl ion concentration. He was of the opinion that this might be the reason why the sulfate liquor attacks the cellulose less. However, since the yield of cellulose is appreciably higher with sulfide-containing liquors than with pure NaOH-solution, one must conclude, that the former exert a protective action even when there is a great excess of alkali. This may possibly be the result of the fact that sodium sulfide removes dissolved oxygen, which is known to exhibit a strong degrading action on cellulose in alkaline solution.

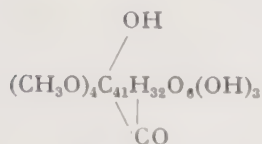
Certainly, the most important reason for the favorable effect, however, is the shortening of the reaction time. Recent investigations by E. Hägglund (21) and his collaborators have indeed shown that the strength is primarily dependent on the cooking time. The time during which the cellulose and the wood polysaccharides are exposed to the action of the alkali must be as short as possible in order to preserve the strength. As has been emphasized before, the cooking time required to reach a given value of the chlorine number decreases with increase in the sulfide content.

It was also found that the chemical attack does not consist of a shortening of the fibers during the cooking. This effect becomes apparent only after beating, for instance in a Hollander beater. Even with a degree of beating corresponding to 20-30° S. R., it was found that the fibers obtained by cooking with a sulfide-free alkali liquor was to a marked degree split into short fragments, whereas a sulfate pulp, obtained by cooking with a liquor containing 40% sulfide, showed practically no such shortening of the fibers. If the beating is carried further, the pulp from pure caustic liquor disintegrates almost completely into short-fiber fragments.

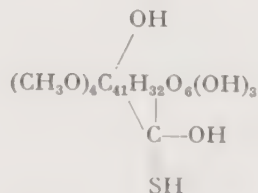
It was further ascertained, in agreement with earlier results, that the cooking of fibrous material which has been more or less split into fibers results in a marked decrease in strength. It is therefore impossible to produce acceptable alkali pulp from so-called Asplund fiber (Defibrator process). Furthermore it is important that the chips shall not be bruised by the knives of the cutting machine.

2. Formation of Thioglignin. Hägglund (22) found that by cooking spruce with a solution of sodium hydrosulfide at, for example, a temperature of 160° C., a considerable amount of sulfur is organically bound in the solid phase. The greatest amount of lignin remains in the wood. The lignin existing in the wood has been changed in composition so that it can, to a considerable extent, be brought into solution under mild conditions, for example, by cooking with 5% sodium hydroxide under atmospheric pressure or by extraction with organic solvents, such as 75 % alcohol. The lignin which has been extracted in this way contains about 8-9% sulfur and about 11% methoxyl. The sulfur containing lignins are called thioglignins. F. E. Hanson (23) has studied the possible reasons for the easy solubility of thioglignins in alkaline solutions. He suggested that the bound sulfur affects the acidic character of the lignin so that it is more easily dissolved by alkali. This, however, is difficult to understand, since carbon dioxide precipitates the lignin of the sulfate black liquor to the same extent as that of soda black liquor.

If one delignifies with sodium sulfide, the greatest part of the lignin goes into solution. Lignin, precipitated from this solution with hydrochloric acid, has a sulfur content of only about 3%. E. Ahlm (24) has investigated this type of lignin. On the basis of methylation and acetylation studies, he has advanced a suggestion regarding the formation of thiolignin which is represented by the following formula:



Native Lignin (Brauns) (25)



Thiolignin (Ahlm)

Thus, thiolignin should originate by the addition of hydrogen sulfide to a carbonyl group in the lignin, whereby a mercaptan and a hydroxyl group are formed. The mercaptan group should give lignin increased acid properties, and this would explain the greater alkali solubility of thiolignin compared with sulfur-free lignin.

The results of the aforementioned two-step cooking procedure sodium hydrosulfide at 160°C and dissolution by cooking with dilute sodium hydroxide cannot be explained by means of Ahlms theory. An 8 to 9% sulfur content in thiolignin would be equivalent to a carbonyl content in lignin which is considerably greater than that which can actually be shown to exist. T. Enkvist and E. Hägglund (26, 27) could not find any appreciable amount of mercaptan sulfur by titration of thiolignin with iodine in alcohol solution, which also is contrary to Ahlms theory. It is now known that mercaptan groups are easily dehydrogenated to disulfide groups even by air, but that these easily reform mercaptans on reduction. Enkvist and Hägglund found, however, that even after such reduction only a very small fraction of the total sulfur content of the thiolignin obtained from cooking with sodium hydrosulfide was present as mercaptan groups. They came to the conclusion that the sulfur in the thiolignin in question is mainly present as sulfide groups.

Hägglund and his colleagues (22, 26, 27, 16) further studied "hydrogen sulfide lignin," which can be obtained by heating resin-free spruce wood at 100°C with a buffered, saturated water solution of hydrogen sulfide at pH 7 and thereafter extracting the wood with organic solvents such as pyridine or 75% alcohol. By repeating this procedure eight times about 60% of the lignin of the wood can be brought into solution. After the eight hydrogen sulfide cooks and pyridine extractions, the undissolved wood

contains 17.1% Klason lignin and 2.11% methoxyl. The wood cannot be reduced to fibers, nor is it swollen. Under a microscope, in ultraviolet light, the compound middle lamella appears very dark, due to the ultraviolet absorption of the lignin (cf. p. 294). In the secondary walls, however, the amount of ultraviolet absorbing material has markedly decreased.

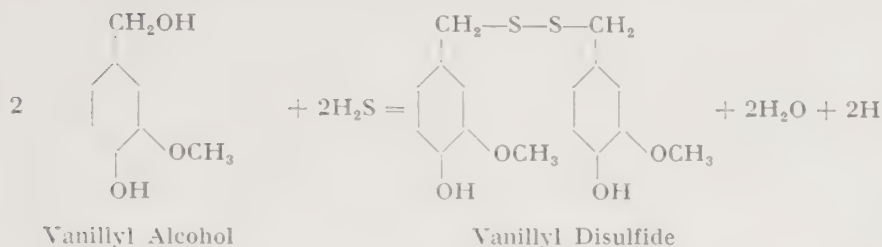
The hydrogen sulfide lignin can be separated with the aid of solvents into several fractions with sulfur contents varying from about 7 to 17% and with methoxyl contents of 12-15%. These lignin fractions contain about 7% of disulfide sulfur, the rest probably being bound in organic monosulfides.

Molecular weights were determined by Rast's method and a method described by M. af Hällström (28), which is based on the principle of isothermal distillation. Both of these methods gave consistent results. For various preparations of thiolignin and sulfur-free alkali lignin, values from 500 to about 3,000 were obtained. There apparently exist several thio- and alkalilignins of different, although not very high, molecular weights.

No solid basis for a belief that isolated thiolignin should be more acid than sulfur-free alkali lignin was obtained from these investigations. The differences in molecular weights are not large enough for one to assume that any essential difference in the rate of diffusion should occur during the cook. The lignin obtained from the black liquor of both soda and sulfate cooks show, to a large extent, similar equivalent and molecular weights. This, nevertheless, does not mean that the lignin cannot behave differently in the two types of cooks during the early phases of the dissolution process.

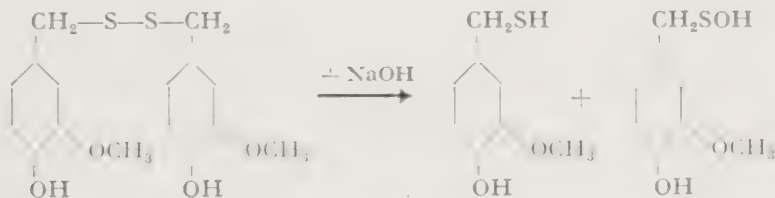
Spruce wood which has been cooked with hydrosulfides or hydrogen sulfide at about 160°C shows, under a microscope in ultraviolet light a peculiar behavior of the lignin, which during the cook is plastified or molten and flows out into the lumen of the cell, in many cases filling it up completely (28 a).

In cooks on model substances for lignin, it was found (29) that the heating of eugenol, isoeugenol, veratrol, and acetoguaiacone (acetovanillone) with hydrogen sulfide in water solution at 100°C and pH 7 gave only minute quantities of sulfur compounds. Vanillin, under the same conditions, remained also mainly unchanged, and even when cooking with sulfhydrate at 160°C, about 15% of the vanillin was recovered. On the contrary, vanillyl alcohol, a model substance known from the sulfite process (30), when cooked with hydrogen sulfide at 100°C and pH 7, gave a good yield of crystalline vanillyl disulfide, whereas with sodium hydrosulfide at 160°C it gave vanillin in a yield of about 10%.

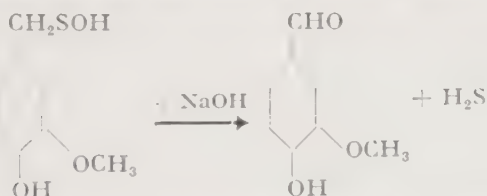


It is to be noted that phenol alcohols, of a similar type as vanillyl alcohol, are intermediate products in the synthesis of phenolformaldehyde resins, such as bakelite, and that these phenol alcohols are known to be easily condensed by alkali to high molecular amorphous resins.

From earlier work (31) it is known that many disulfides are decomposed by heating with alkali to one molecule of mercaptan and one molecule of sulfenic acid. Vanillyl disulfide has been shown (29) to react in a similar way:



The sulfenic acid, in the presence of sodium hydroxide, splits off hydrogen sulfide and gives the corresponding carbonyl compound.



In the case of vanillyl disulfide, such a reaction occurs to at least 50% of the disulfide. It is very possible that carbinol groups adjacent to the benzene nucleus in the lignin react in a similar manner. Indeed, hydrogen sulfide lignin in alkaline solution splits off about half its sulfur as hydrogen sulfide. A difference is that this occurs at a considerably higher temperature (about 160°C) than for vanillyl disulfide.

Hydrogen sulfide lignin takes up no, or almost no, methoxyl upon treatment with methanol and hydrogen chloride, but takes up two new methoxyl groups for every four earlier present in the lignin upon treatment with diazomethane.

Determinations of the equivalent weight of sulfur-free alkali lignins have been carried out by two methods. The first one was a poten-

tiometric titration of the lignin in ethylene diamine solution. In the other method, the lignin was dissolved in a definite amount of 0.1 N sodium hydroxide and a solution of barium chloride was added, which caused the lignin to precipitate as a salt. The amount of unreacted alkali was determined by titration. The following table shows the values obtained:

Lignin obtained by Treatment of Spruce Wood with	NaOH, 160° C 16 hours	Na ₂ S, 160° C 3 hours		NaSH, 160° C 16 hours		H ₂ S, 100° C, 72 hours			
Fraction Soluble in	Etha- nol	Etha- nol	Ether	Etha- nol	Dioxan	Ether	Etha- nol	Etha- nol	Etha- nol
Sulfur content in lignin, %	0	3.77	3.24	6.16	5.27	12.09	8.82	7.23	8.98
Equivalent weight: BaCl ₂ -method . .	190	223		238	232	281		347	
Ethylenediamine method	200		192	200			372		321

Obviously, both methods show that the equivalent weight for the lignin from strong alkali cooks is about 200, which approximately corresponds to a lignin building unit of 10 carbon atoms. Hydrogen sulfide lignin, on the other hand, has a somewhat higher equivalent weight.

Thiolignins, isolated from common sulfate black liquors and containing about 2% of organically bound sulfur, react easily with diazomethane; they show low equivalent weights on titration with alkalies and contain no mercaptan groups. These facts tend to indicate that such sulfate lignins contain substantial amounts of phenolic, or possibly enolic, hydroxyl groups. Recent investigations (31a) on the ultraviolet absorption spectra also seem to indicate that sulfate lignins contain a great number of phenolic hydroxyl groups (shift of absorption maxima towards longer wave lengths on the addition of alkali to alcoholic solutions). On the contrary, hydrogen sulfide lignins, prepared from spruce wood at 80° C and neutral reaction, contain considerably smaller quantities of such hydroxyl groups. Equivalent weight determinations carried out on vanillyl disulfide (as a model substance) according to the above barium chloride method showed that, under the conditions used, not only phenolic hydroxyls but also the disulfide grouping itself consumes alkali. Thus, it seems possible that the alkali consumption of the hydrogen sulfide lignins prepared at neutral reaction is due in part to a reaction of the disulfide grouping. These lignins, on heating with solutions of sodium hydroxide, are easily transformed, already at 80° C, into thiolignins with a great number of phenolic hydroxyls.

On the basis of the related investigations, the following hypothesis for understanding the part played by the sulfidity in the sulfate cook has been advanced: During the sulfate cook, the lignin, in the solid phase, first takes up sulfur. It is believed that the hydroxyl groups in substituted benzyl alcohol groups are replaced by mercaptan groups. These are, however, not stable in alkaline solution, but are converted partly into sulfide groups by reacting with a hydroxyl group from either the same or another molecule. Another part is dehydrogenated, probably by disproportionation reactions, to disulfide compounds. Besides of these sulfidization reactions a hydrolytic splitting of the lignin under the action of alkali takes place. In this manner free phenolic hydroxyl groups are formed, and the lignin becomes soluble in alkali. Furthermore, the disulfide compounds are split under the influence of alkali into the corresponding mercaptans and sulfenic acids. The hydrogen sulfide, which is then split off from this acid, can react again with more lignin. The mercaptan, in its turn, can react further, being converted into sulfide and disulfide. By means of the sulfidization, a condensation-sensitive group is blocked, and thus condensation of the lignin in the wood residue is inhibited. Such a condensation is very possibly the reason for the fact that the lignin remaining in the wood in a sulfide-free alkali cook becomes more difficult to dissolve.

D. DEMETHYLATION OF LIGNIN AND FORMATION OF LOW-MOLECULAR FISSION PRODUCTS

Methyl alcohol and methyl mercaptan are formed as by-products in sulfate pulping (cf. p. 490). This, and the fact that the methoxyl content of alkali lignin is less than that of the lignin in the wood, makes it highly probable that a splitting of methoxyl groups occurs during the cook. The yields of the said by-products and the diminution of the methoxyl content of the lignin are, however, so small, that they alone cannot explain the low value, about 200, for the equivalent weight of alkali lignin, even if one assumes that the reaction leads quantitatively to the liberation of phenolic hydroxyl groups. There must be other reactions, resulting in the liberation of acidic, probably phenolic, groups in the lignin (cf. p. 486).

Substances, which probably are demethoxylation products of lignin, have been found in the black liquors (32). As is seen from the table on p. 476, a considerable part of the lignin cannot be precipitated by acids from the black liquor from alkaline pulping. This "water soluble lignin" occurs in all types of black liquors from cooks with spruce to an amount of about 7% of the wood weight, that is, about 25% of the amount of lignin. If one cooks with sodium hydrosulfide at 160°C. a liquor is obtained, from which no lignin can be precipitated by hydrochloric acid. It

is all "water soluble." Some of this "water soluble" lignin precipitates, on evaporation in a hydrochloric acid solution or upon the addition of concentrated hydrochloric acid, as an amorphous substance which, after purification, contains 9.4% ash, 11.9% organically bound sulfur, and 7% methoxyl groups. Elementary analysis and calculation for ash-free substance gives the formula: $C_9H_{9.3}O_{2.2}S_{0.7}(OCH_3)_{0.4}$. Thus, the substance is poor in methoxyl and rather rich in sulfur. Its yield amounts to 4% of the wood.

H. Schwartz, J. McCarthy, and H. Hibbert (33), in connection with studies of the lignin remaining in kraft pulp (34), investigated a water soluble product obtained from black liquor after sulfate cooking of Slash pine. This product contained 7% methoxyl groups and was considered by the above authors to be a degradation product of lignin.

When black liquor from hydrosulfide cooks on spruce wood was methylated with dimethyl sulfate, neutralized, and extracted with ether, acetoguaiacone (acetovanillone) and its methylation product, acetoveratrone, could be isolated with a total yield of 0.9% of the wood (32). Neither vanillin nor other aldehydes could be found. The liquor from a cook on spruce with pure sodium hydroxide contained some vanillin (0.05%), but no acetoguaiacone, whereas black liquor from a sulfate cook contained both substances, the yield of acetoguaiacone amounting to about 0.1%. The yield of acetoguaiacone seems to be dependent of the sulfidity of the cooking liquor.

After cooking aspen wood with sodium hydrosulfide at 180°C, D. L. Brink, R. L. Hossfeld and W. M. Sandstrom (35) isolated from the black liquor phenol, o-cresol, pyrocatechol, and acetoguaiacone (acetovanillone).

E. ALKALI COOKS WITH ADDITION OF OTHER SULFUR CONTAINING REAGENTS THAN SODIUM HYDROSULFIDE

M. Bray and B. Singer, in sulfate pulping experiments on Engelman spruce, came to the conclusion that both sodium sulfite and sodium thiosulfate are active pulping agents, and that the most advantageous results are obtained when half of the sulfide present in conventional sulfate cooking liquors is replaced by sulfite or thiosulfate (36, 37).

The addition of small amounts, 1-2% of the wood, of elementary sulfur to sodium hydroxide cooking liquors has been shown (38) to result in a marked decrease in bleach consumption as well as in an improvement in pulp qualities.

Preliminary results from orienting experiments by E. Hägglund and T. Johnson (39) concerning the addition of elementary sulfur in considerable quantities to sulfide containing white liquors are seen in the following table.

Sodium Sulfide Content of White Liquor (% of Active Alkali)	Sulfur Addition g./l.	Cooking Time at 170° (hrs.)	Yield (% of Weight of Wood)	Roe- Chlorine Number
0 (Pure alkali cooking).....	0	5	51.4	11.0
10 (Equivalent to 2.25 g. S/l.)	0	3	49.5	5.6
0.....	2.25	3	52.4	5.9
30 (Equivalent to 6.75 g. S/l.)	0	2	50.3	5.5
0.....	6.75	2	53.0	5.8
10.....	2.25	2	53.0	6.2
10.....	4.50	2	54.0	5.2
10.....	7.75	2	55.1	6.2

In this series of experiments, white liquor prepared from pure chemicals was used, but the same results were obtained on addition of 50% of black liquor. The definitely higher yield of pulp on cooking with sulfur addition as compared with that obtained with an equivalent addition of sodium sulfide is noteworthy. As far as strength is concerned, the addition of sulfur appears to act exactly like an increase in the sulfide content.

F. EFFECT OF PREHYDROLYSIS OF WOOD IN ALKALINE PULPING

Sulfate pulps have thus far been used almost exclusively for various types of paper. They were not suitable for rayon probably on account of their high pentosan content. As a matter of fact, it has been found useful to carry out an hydrolysis with dilute mineral acid (at elevated temperature and pressure) before the alkali cooking (3). This pretreatment has an especially favourable effect with hardwood, straw, and other raw materials rich in pentosan. The high yield of α -cellulose with this treatment is remarkable. The bleaching of such pretreated alkali pulps is also reported to be easier. G. Jayme and P. Schorning (40) have proposed carrying out the initial hydrolysis with 10-20% sulfuric acid, in order to obtain furfural from the materials rich in pentosan. Th. Ploetz (41) suggests hydrolyzing the wood polysaccharides with hot, dilute acids by "percolation" and dissolving the cellulose in the residue with ammoniacal copper oxide, or as viscose. This would certainly not yield a particularly pure solution of cellulose.

Attempts to cook sulfite pulp first with 0.1 N hydrochloric acid and then to refine with alkali were enlightening as to the mode of action of the acid pretreatment of wood. An improvement in the resulting pulp by the use of hydrochloric acid was not observed; on the contrary, an impairment occurred as compared with alkali treatment alone. The content of wood polyoses did not decrease appreciably, and the α content was less than that of the starting material. The reason, according to E. Correns (42), is that the cellulose is greatly degraded by acid treatment of the pulp. In the isolated fibers which have been freed of lignin, the acid acts on the

cellulose and damages it, but in the intact wood the cellulose is protected by the lignin, and only the wood polysaccharides are attacked.

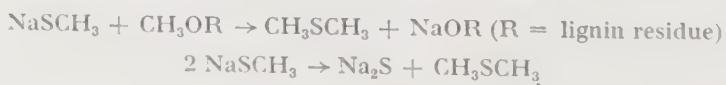
It is debatable if such a protection by the lignin exists. It is true, in any case, that isolated fibers, whether they contain lignin or not, lose their strength relatively easily on treatment with the usual pulping liquors (bisulfite or caustic) used in wood pulp manufacture. Even during alkaline cooking in rotary digesters, where mechanical disintegration into fibers can occur before the chips are fully digested, the alkali has such a strong effect on the exposed fibers that their strength is very much affected (43, 44).

G. SULFATE COOKS OF HARDWOODS

Sulfate cooking of hardwoods is by now practiced to a considerable extent in Scandinavian countries (44 c). M. W. Bray and J. S. Martin (44 a) studied the sulfate pulping of sweetgum (*Liquidambar styraciflua*). Orienting investigations concerning sulfate cooks on various American hardwoods were made by L. W. Forman and D. D. Niemeyer (44 b). The best yields and strengths of the pulps were obtained from the following hardwoods: swamp red oak (*Quercus shumardii*), swamp Spanish oak (*Quercus pagoda*), wild olive tree (*Halesia carolina*), scarlet oak (*Quercus coccinea*), yaupon (*Ilex vomitoria*), pin oak (*Quercus palustris*), Southern red oak (*Quercus rubra*), loblolly bay (*Gordonia lasianthus*), and laurel oak (*Quercus laurifolia*). Lignin poor pulps were obtained from these woods in yields of more than 45% of the wood weight. The bursting and tensile strengths were comparatively good, but the tear strength, as could be expected, was low.

III. The By-Products of the Alkaline Pulping Processes

During the alkaline digestion a portion of the methoxyl groups of the wood are split off. When only sodium hydroxide is used in the cooking, this results in the formation of methyl alcohol exclusively. Cooking with sulfate liquor yields, in addition, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Dimethyl sulfide can be formed from sodium mercaptide by the following reactions, according to Klason:



Part of the methyl sulfur compounds are to be found in the condensate from the waste gases, along with larger or smaller quantities of turpentine

oil, methyl alcohol, etc. (46). The following analysis of the condensate by H. Falk may be noted (45):

Products in Condensate	Per Ton of Pulp from Pine Wood kg.	
	In Oil Fraction	In Aqueous Fraction
Mercaptan.....	0.062	0.06
Dimethyl sulfide.....	0.927	0.17
Dimethyl disulfide.....	0.103	0.05
Turpentine oil.....	8.472	0.92
Residue on distillation.....	0.721	—
Methyl alcohol.....	—	5.00
Ammonia.....	—	0.18

The resin acids and fatty acids of the wood go into solution as sodium salts during the alkaline cooking. The soap rises to the surface in the containers in which the black liquor is collected, and forms a viscous dark brown mass, the raw soap. The solubility of the soap in the black liquor is decreased by addition of concentrated black liquor. The soap is skimmed off, cooked with 40% sulfuric acid, and the mixture of oil and sodium sulfate solution is separated. The oil, called tall oil, is washed with warm water and dried by heating. The following composition is typical of the tall oil obtained in Northern Sweden:

	°.
Water.....	0.5- 2
Unsaponifiabiles.....	8-11
Resin acids.....	35-45
Fatty acids.....	45-55

The tall oil so obtained can not be worked up immediately into useful products; for this purpose it must be purified first. In this purification one attempts to remove the odoriferous components and those which impart a dark color, to decrease the content of unsaponifiabiles, and to separate the resin acids from the fatty acids.

The most effective purification of the tall oil is obtained by fractional vacuum distillation with superheated steam (47).

The first fraction consists of oil which contains much palmitic acid as well as highly unsaturated neutral oil, which has been called "chill mold oil" because it is used for coating chill molds (18). The main distillate fractions are a fatty acid and a resin acid fraction. The fatty acid fraction consisting chiefly of oleic acid plus palmitic and linoleic acids (49), is worked up into soap and soft soap, and also partly into emulsifying agents [a substitute for Turkey-red oil (50)] by treatment with sulfuric acid. The resin acid fraction crystallizes, the crystals are centrifuged off and marketed as a substitute for colophony, which is used (among other things) for sizing paper. The residue from the distillation, the tall oil pitch (formerly called sulfate pitch), constitutes about 25%. It is used in

the chemical industry as a raw material for making, among other things, black printing ink, varnish, and sizing for kraft paper and wallboard.

The yield of raw tall oil amounts to about 25-80 kg. per ton of pulp, when only pine wood is used. Of this, the main oil fraction of the distillate and the crystallized resin acids together constitute 60-70%.

For intensive investigations of tall oil we are indebted particularly to E. Larsson (51), H. Bergström (52), H. Sandqvist (53), M. Dittmer (54), and T. Hasselström (55). Bibliographies on the large field of tall oil research are given by *l.a.* T. Jakobson (56) (763 references) and C. J. West (57). The composition of tall oil and its distillation products has been reviewed by C. O. Gabrielson (57a). Reviews on possible uses of tall oil have been given by L. Byman (58), W. Jennings (58a) and in Tappi (58b).

A phytosterol (59) and lignoceryl alcohol were found in the unsaponifiable part of the tall oil, while the remainder consisted mainly of hydrocarbons. Canadian tall oils seem to contain more phytosterol than the Scandinavian ones (60).

In the last few years much attention has been devoted to the separation of resin acids and fatty acids. Among other things, the proposal has been made to cook the tall oil with methyl, ethyl, or other alcohols and sulfuric acid, and then to extract with sodium hydroxide, after addition of solvents, such as petroleum fractions. By this treatment the resin acids are converted into sodium soaps, and the fatty acids into distillable and easily hydrogenated esters (61). Even without esterification it is said to be possible to effect at least an approximate separation of resin acids from fatty acids by extraction with two mutually insoluble liquids, or by other means (58). These methods have not yet been shown to be more advantageous than distillation.

Turpentine and methyl alcohol are to be mentioned among other by-products. The digestion of pine wood yields about 8 kg. of raw turpentine per ton of pulp, or somewhat more than 5 kg. of purified turpentine. The impure sulfate turpentine (sulfate oil) is purified by fractional distillation and by washing with sulfuric acid and sodium hydroxide. A lighter pinene fraction and a heavier carene fraction are thus obtained (62); the latter is sometimes used for making toluene, and the former in the varnish and dye industries. Various alcohols can be added to the ethylene linkages in terpenes; this reaction leads to the formation of ethers, which can be used as solvents or plasticizers (63). Several kinds of lacquers and varnishes can be obtained by the addition of maleic anhydride, phenols, or phenol-formaldehyde resins to the terpenes (64).

It is absolutely necessary, for economic reasons, to recover the alkali from the salts present in the black liquor. This is done by evaporating,

calcining, and then leaching out in the soda pulp process, or by combustion and melting in the sulfate process. The salts thus freed of organic matter are causticized with lime. Thus far, the aim in practical operation has been to carry out the alkali regeneration in a manner as economical in the use of heat as possible.

There has been no dearth of proposals and attempts to obtain valuable materials during the regeneration of the alkali. In this connection the process worked out by E. L. Rinman (65) should be mentioned. In this procedure, the black liquor is evaporated completely, and then submitted to a dry distillation after a further addition of lime, or in some cases, baryta. Acetone and methyl alcohol begin to be formed at 250° C. The "soda charcoal," the mixture of charcoal and inorganic substances which remains after the distillation, is leached, and the soda converted into caustic. The residue of charcoal and calcium carbonate thus formed, is burnt and the chalk converted into quicklime.

According to a report by E. Heuser (66), the actual technical yields per ton of pulp were as follows:

	kg.
Methyl alcohol.....	10
Acetone.....	8
Butanone (methyl ethyl ketone)....	10
Ketone oils.....	6
Light oil.....	4
Heavy oil.....	52

Appreciably higher yields were reported by E. L. Rinman (65), viz. 25-30 kg. methyl alcohol, 16-20 kg. acetone, 16-20 kg. methyl ethyl ketone, 18 kg. ketone oils and 50 kg. of heavy oils.

D. Johansson (67) made a more thorough investigation of the chemical processes involved in Rinman's alkaline dry distillation of black liquor. He confirmed Rinman's finding that the addition of alkali before distilling increases the yield of acetone and butanone. Dry distillation of the lignin portion with steam under the same conditions caused approximately half of the methoxyl to be split off as methyl alcohol. The hydroxy acids of the liquor yielded, besides much hydrogen, mainly salts of fatty acids, such as acetate and propionate. Small quantities of methyl and ethyl alcohol were also formed. Further heating caused the formation of acetone, butanone, and acetone oils, among other things. The yield of acetone, as might be expected, decreased greatly when there was an excess of alkali.

Attempts to obtain by-products have also been made in the United States (68) along the lines of Rinman's work. A. H. White and J. D. Rue (69) reported such attempts, made on both small and large scales. They obtained from 1 cord of wood (3.624 cu.m.) 0.9 gallons (3.4 l.) of acetone

and 6 gallons (22.7 l.) of methyl alcohol. Thus far, Rinman's procedure has not become of technical importance.

E. Hägglund and F. Bergius (70) have discovered a regeneration procedure for the black liquor alkali, which differs in principle from those mentioned above. The black liquor is heated in a continuous process (71) to a temperature of 350° C., corresponding to a pressure of 200 atm. In the course of several minutes the organic material is decomposed yielding chiefly tar, gases, methyl alcohol, acetone, and acetic acid. The yield depends on the experimental conditions. The type of wood also plays an important role. Since the gas is chiefly hydrogen, a hydrogenation under pressure certainly occurs here (72). Similar experiments were later carried out by H. Wallin and S. Odén (73). The results of Hägglund's and Bergius' work were confirmed.

Systematic investigations of the pressure heating of black liquor have been carried out by E. Hägglund, M. Tuominen, and K. Lindblom (74). The following yields were obtained:

Raw Material	Tar g./100 g. Material	Methanol g./100 g. Material	Acetone g./100 g. Material	Acetic Acid g./100 g. Material	Gas l./100 g. Material
Pine.....	25	2.5	—	5-6	4.5
Aspen.....	16	2.8	0.45	9.25	6
Beech.....	19	2.0	—	9.8	6.5
Birch.....	18	1.6	—	10.0	6
Rye straw.....	21	1.0	—	7.5	6.5
Esparto.....	17.5	1.5	0.5	8.0	4.0

The yield, especially in the cases of tar, methanol, and gases, is to a large degree dependent on whether or not alkali (e. g., NaOH) is added to the waste liquor before heating under pressure.

REFERENCES

1. Watt, C., and Burgess, H., U. S. Pat. 1,448, 1,449 (1854).
2. Cf. Kirchner, E., *Das Papier*, part III, vol. C, Biberach, 1907.
3. Dorr, R. E., *Papierfabr.* **37**, 1 (1939); **39**, 267 (1941); *Kunstseide u. Zellwolle* **22**, 278 (1940); *Svensk Papperstidn.* **46**, 361 (1943).
4. Klason, P., *Tekn. Tid. Uppl. C., Kemi* **23**, 33 (1893).
5. Hägglund, E., *Cellulosechemie* **5**, 81 (1924).
6. Cf. Rinman, E. L., *Papierfabr.* **10**, 39, 101 (1912); *Swensk Kem. Tidskr.* **23**, 163 (1911).
7. Sutermeister, E., *Chemistry of Pulp and Paper Making*, New York, 1920, p. 124.
8. Christiansen, C., *Ueber Natronzellstoff*, Berlin, 1913, p. 64.
9. Hägglund, E., *Finnish Paper Timber J.* **5**, 361 (1925).
10. Brauns, F. E., and Grimes, W. S., *Paper Trade J.* **108**, No. 11, 40 (1939).

11. Wells, S. D., Grabon, R. H., Staidl, J. A., and Bray, M. W., *Paper Trade J.* **67**, No. 24, 49 (1923); **87**, No. 23, 64 (1928); Hägglund, E., *Finnish Paper Timber J.* **5**, 361 (1925); Bruun, J., *Medd. Vetenskapsakad. Nobelinst.* **6**, No. 10 (1924); Arrhenius, S., *Zellstoff u. Papier* **4**, 183 (1924); *Paper Trade J.* **82**, No. 15, 65 (1926); Schmidt-Nielsen, S., and Overwien, T., *Papir-J.* **15**, 9 (1927); Lewis, H. F., and Laughlin, E. R., *Paper Trade J.* **91**, No. 25, 57 (1930); Ross, J. H., *Pulp Paper Mag. Can.* **29**, 482 (1930); Adlington, W. E., and Ross, J. H., *Pulp Paper Mag. Can.* **32**, 248 (1932); Macklin, L. S. and Maass, O., *Can. J. Research* **7**, 451 (1932); Bray, M. W., and Curran, C. E., *Paper Trade J.* **97**, No. 5, 30 (1933); Hägglund, E., and Eidem, L., *Svensk Papperstidn.* **36**, 632 (1933); Martin, J. S., Bray, M. W., and Curran, C. E., *Paper Trade J.* **97**, No. 20, 38 (1933); Nolan, W. J., and McCready, D. M., *Paper Trade J.* **102**, No. 4, 36 (1936); Bray, M. W., Martin, J. S., and Schwartz, S. L., *Paper Trade J.* **105**, No. 24, 39 (1937); **109**, No. 17, 40, No. 18, 29 (1939); Schwartz, S. L., and Bray, M. W., *Paper Trade J.* **107**, No. 12, 24 (1938); Larocque, G. L., and Maass, O., *Can. J. Research* **19B**, 1 (1941); Basberg, A., *Papir-J.* **29**, 99, 109, 119 (1941).
12. Hägglund, E., and Hedlund, R., *Papierfabr.* **30**, 49, 61 (1932).
13. Kullgren, C., *Ing. Vetenskapsakad. Handl.*, No. **65** (1927).
- 13 a. Koelichen, K., *Z. physik. Chem.* **33**, 129 (1900).
14. Arrhenius, S., *Medd. Vetenskapsakad. Nobelinst.* **6**, No. 10 (1924).
15. Kullgren, C., *Papierfabr.* **24**, 20 (1926).
- 15 a. G. Martin, *Tappi* **33**, 48 (1950).
16. Hägglund, E., *Tappi* **32**, 241 (1949).
17. Heuser, E., *Wochbl. Papierfabr.* **44**, 2209 (1913).
18. Klason, P., *Wochbl. Papierfabr.* **39**, 3859, 3963 (1908).
- 18 a. Borlew, P. B., and Pascoe, T. A., *Paper Trade J.* **122**, No. 10, 31, **123**, No. 15, 178 (1946).
19. Klason, P., and Segerfelt, B., *Arkiv Kemi, Mineral. Geol.* **4**, No. 6 (1911).
20. Anderzén, O., and Holmberg, B., *Ber.* **56**, 2044 (1923).
21. Hägglund, E., *Svensk Papperstidn.* **48**, 195 (1945).
22. Hägglund, E., *Svensk Papperstidn.* **44**, 183 (1941).
23. Hanson, F. E., *Paper Trade J.* **112**, No. 2, 32 (1941).
24. Ahlm, E., *Paper Trade J.* **113**, No. 13, 115 (1941).
25. Brauns, F. E., *Paper Trade J.* **11**, No. 14, 33 (1940).
26. Enkvist, T., and Hägglund, E., Jubilee vol. J. A. Hedvall, Goteborg, 1948, p. 149.
27. Enkvist, T., *Svensk Papperstidn.* **51**, 225 (1948).
28. af Hällström, M., *Ann. Acad. Sci. Fennicae* **A34**, No. 5 (1931); **40**, No. 6 (1934).
- 28 a. Enkvist, T., Moilanen, M., and Alfredsson, B., *Svensk Papperstidn.* **52**, 513 (1949).
29. Enkvist, T., and Moilanen, M., *Svensk Papperstidn.* **52**, 183 (1949).
30. Lindgren, B. O., *Acta. Chem. Scand.* **1**, 779 (1947).
31. Schöberl, A., *Angew. Chem.* **53**, 227 (1940).
- 31 a. Enkvist, T., unpublished work.
32. Enkvist, T., Moilanen, M., and Alfredsson, B., *Svensk Papperstidn.* **52**, 53 (1949).
33. Schwartz, H., McCarthy, J., and Hibbert, H., *Paper Trade J.* **111**, No. 18, 30 (1940).
34. Kuettel, G. M., Thesis, Wisconsin, 1933; Holzer, W. F., *Paper Trade J.* **99**, No. 12, 91 (1934); Bard, J. W., *Paper Trade J.* **113**, No. 12, 29 (1941).
35. Brink, D. L., Hossfeld, R. L., and Sandstrom, W. M., *J. Am. Chem. Soc.* **71**, 2275 (1949).
36. Bray, M., and Singer, B., *Paper Trade J.* **125**, No. 8, 49 (1947).

37. Cf. Aronovsky, S. I., *Paper Ind.* **16**, 413 (1934); Aronovsky, S. I., and Gortner, R. A., *Ind. Eng. Chem.* **22**, 941 (1930); **25**, 305, 1260 (1933).
38. Bray, M. W., Martin, J. S., and Carpenter, L. A., *Paper Trade J.* **93**, No. 12, 33 (1931); Spence, G. K., *Paper* **27**, No. 1, 19 (1920); Wells, S. D., *Paper Ind.* **5**, 786 (1923).
39. Hägglund, E., and Johnson, T., *Svensk Papperstidn.* **49**, 204 (1946).
40. Jayme, G., and Schorning, P., *Holz Roh- u. Werkstoff* **3**, 273 (1940).
41. Ploetz, Th., *Holz Roh- u. Werkstoff* **4**, 380 (1941).
42. Correns, E., *Angew. Chem.* **54**, 363 (1941); *Cellulosechemie* **19**, 105 (1941).
43. Hägglund, E., *Svensk Papperstidn.* **38**, 145 (1935).
44. Jayme, G. *Chem. Ztg.* **66**, 89 (1942).
- 44 a. Bray, M. W., and Martin, J. S., *Tech. Assoc. Papers* **24**, 251 (1941).
- 44 b. Forman, L. V., *Paper Trade J.* **118**, No. 12, 27 (1944); Forman, L. V., and Niemeyer, D. D., *TAPPI Monograph Series* No. 4 (1947) 167.
- 44 c. Jensen, W., *Paper and Timber* **33B**, 4 (1951).
45. Falk, H., *Papierfabr.* **7**, 469 (1909).
46. Hägglund, E., Natronzellstoff. Technik u. Praxis d. Papierfabrikation II, 2, 243 (1926); cf. Bergström, H., *Papierfabr.* **11**, 427 (1913); Bergström, H., and Trobeck, K. G., *Svensk Papperstidn.* **48**, 49 (1945); Hägglund, E., and Hedlund, R., *Svensk Papperstidn.* **36**, 258 (1933); Halse, O., and Dedichen, H., *Ber.* **50**, 623 (1917).
47. Hellström, A., *Tekn. Fören. i Finland Förh.* **36**, 215 (1916); *Paper Ind.* **17**, No. 3 (1935).
48. Göthner, I., *Svensk Papperstidn.* **45**, 169 (1942).
49. Sandström, G., and Sandström, M., *Svensk Papperstidn.* **47**, 381 (1944); Anderson, R. H., and Wheeler, D. H., *Oil and Soap* **22**, 137 (1945).
50. Noerdlinger, H., German Pat. 310,541 (1919).
51. Larsson, E., *Svensk Kem. Tid.* **17**, 148 (1905).
52. Bergström, H., *Jernkontorets Ann. Proceedings* **9**, 575, 649 (1908); **12**, 507 (1911); *Papierfabr.* **11**, 73 (1913); *Svensk Papperstidn.* **35**, 156 (1932); **48**, 551 (1945).
53. Sandqvist, H., *Ing. Vetenskapsakad. Handl.* No. 10 (1922).
54. Dittmer, M., *Z. angew. Chem.* **39**, 262 (1926).
55. Hasselström, T., McPherson, J., and Hopkins, S., *Paper Trade J.* **114**, No. 4, 41 (1940); Hasselström, T., *Paper Trade J.* **118**, No. 16, 30 (1944).
56. Jakobson, T., *Svensk Papperstidn.* **42**, 473, 513, 534, 600 (1939); **43**, 24, 44, 65, 108, 175 (1940); **46**, 128, 183, 283 (1943); **47**, 473, 492, 580, 605 (1944); **52**, 193, 290, 379, 451, 481 (1949); **53**, 369, 444 (1950).
57. West, C. J., *A Bibliography of Tall Oil*, Appleton, Wisconsin, 1942; Supplem. 1945, 1948.
- 57 a. Gabrielson, C. O., *Iva* **21**, 162 (1950).
58. Byman, L., *Paper Trade J.* **123**, No. 22, 35 (1946).
- 58 a. Jennings, W., *Paper Trade J.* **120**, No. 19, 41 (1945).
- 58 b. Anon., *Tappi* **33**, No. 1, 76A, No. 2, 58A (1950).
59. Sandqvist, H., and Hök, W., *Svensk Kem. Tid.* **42**, 106 (1930); Sandqvist, H., and Lindström, T., *Tek. Tid., Uppl. C Kemi* **60**, 41 (1930); Sandqvist, H., and Bengtsson, E. R., *Ber.* **64**, 2167 (1931); Sandqvist, H., Gorton, J., and Bengtsson, E., *Ber.* **64**, 2172 (1931); Barton, D. H. K., and Jones, E. R. H., *J. Chem. Soc.* **1943**, 599.
60. Burch, B. G. N., Shaw, A. C., and Nicholls, R. V. V., *Pulp Paper Mag. Can.* **48**, Convention No., 127 (1947).

61. Öl- u. Fettchemie Ges., Brit. Pat. 278,697 (1927).
62. Skärblom, K., and Linder, Å., *Tek. Tid., Uppl. C Kemi* **67**, 25 (1937).
63. Norton, G. S., *Paper Trade J.* **120**, No. 7, 36 (1945); Powers, P. O., *Paper Trade J.* **126**, No. 5, 39 (1948).
64. Hultsch, K., *Angew. Chem.* **51**, 920 (1938).
65. Rinman, E. L., *Svensk Papperstidn.* **26**, 158 (1923).
66. Heuser, E., *Papierfabr.* **21**, 325 (1923).
67. Johansson, D., *Ing. Vetenskapsakad. Handl.* No. 61 (1927).
68. Drewsen, V., U. S. Pat. 1,298,479, 1,298,480 (1919); White, A. H., U. S. Pat. 1,374,889 (1921).
69. White, A. H., and Rue, J. O., *Met. Chem. Eng.* **16**, 182 (1917).
70. Hägglund, E., and Bergius, F., German Pat. 311,933 (1917); Hägglund, E., U. S. Pat. 1,680,540 (1928); 1,772,216 (1930); 1,795,557 (1931); cf. Winqvist, N., French Pat. 846,776 (1939); Brit. Pat. 528,786 (1940).
71. Hägglund, E., *Papierfabr.* **23**, 493 (1925).
72. Cf. Lautsch, W., *Cellulosechemie* **19**, 86 (1941).
73. Wallin, H., and Odén, S., *Ing. Vetenskapsakad. Handl.* No. 54 (1926).
74. Hägglund, E., Tuominen, M., and Lindblom, K., *Finnish Paper Timber J.* **13**, 508, 569 (1931).

CHAPTER VII

OTHER METHODS OF PULPING

I. Semichemical Pulping

The problem of obtaining pulp in higher yields than are obtained by normal sulfite or sulfate cooking methods has been dealt with repeatedly. During the last years, however, successful efforts to solve this problem have been made, chiefly in America. Production of such high-yield pulp on commercial scale is already existent and steadily increasing. The fact that hardwoods can be utilized very favorably for this kind of pulp is of great importance, because of the ever-decreasing supply of softwoods for pulping.

B. C. Tilghman (1), inventor of the sulfite process, had already in 1867 pointed out that for the production of paper it is not necessary to start out with pulps of low lignin content. Another pioneer of the sulfite industry, A. Mitscherlich (2), also occupied himself with this problem. He patented a method of softening wood chips with sulfurous acid or bisulfite solutions and fiberizing the product thus obtained.

Acid digestion followed by grinding was also used by C. G. Schwalbe and N. F. Hagström (3, 4). They cooked the chips at low temperatures, 95-120°C, with a calcium bisulfite liquor and then drew off the excess. The residue still contained three times as much liquor as the wood originally weighed. The temperature was then raised to not over 145°C and the resulting pulp was defiberized mechanically.

The acid digestion method has not become widely adopted. The interest has the more been directed toward the use of alkaline or neutral digesting agents, chiefly sodium sulfite. As early as 1880, C. F. Cross (5) patented a cooking procedure using this chemical.

E. P. McKeeffe and L. Bradley examined the problem of pulping wood with a digesting liquor containing sodium sulfite with or without a regulated amount of other sodium salts, and the method was carried out on a commercial scale known as the "Keebra" process (6). The advantages of the process were reported to be that the yield and quality of the pulp

were appreciably improved (7). Among the several modifications of this process, the so-called "semi-Keebra" process may be mentioned. In this process a mixture of chiefly sodium hydroxide and sodium sulfite was used. No novel principle was involved as Schacht (8) had already in 1900 patented the use of these agents. The recovery of the chemicals from these processes, however, was very involved and cumbersome.

Neutral sodium sulfite has been found to be the superior pulping agent for the production of high-yield, semi-delignified pulps—commonly called "semichemical" pulps since chemical as well as mechanical treatment is applied. This process has been thoroughly studied at the Forest Products Laboratory in Madison (Wis). J. D. Rue, S. D. Wells, F. G. Rawling and J. A. Staidl (9), of the above-mentioned laboratory, developed a process of making neutral sulfite semichemical pulp, and this method is now applied commercially. Wood chips are cooked in rotary or stationary digesters with a solution of sodium sulfite with sodium bicarbonate or soda as buffering agent. The ratio of sodium sulfite to sodium bicarbonate is 3:1. Chemicals in an amount of 7-15 percent are added depending upon the kind of wood used. Lately efforts have been made (in commercial practice) to use a separate impregnation stage—using an excess of liquor, and removing the surplus of chemicals when the absorption is sufficient. Such a procedure has many advantages. Cooking temperature is 150-170° C., the cycle is 4-6 hours and the yield 70-85 percent. Reuse of liquor has not proved to be practicable. Rod mills and refiners of different types are used for the fiberizing and refining of the softened chips.

The important question regarding the technical recovery of the expensive chemicals must, at present, be considered unsolved, but much research is being done and several methods have been proposed and patented. It should also be pointed out, that the stream pollution caused by waste liquors from the production of neutral semichemical pulp is small compared to that from the manufacture of sulfite pulp. The biochemical oxygen demand of the waste liquor from neutral semichemical pulp is only one fifth that of the liquor from sulfite pulp, per ton of pulp.

The use of non-buffered sodium sulfite as well as conventional chemicals—acid sulfite, soda, and sulfate—for the production of semichemical pulps has likewise been studied (10), and is now applied in commercial production. In some instances waste or black liquors have been used.

Several methods of continuous production of semichemical pulp have been patented (11). The processes consist of a brief treatment of the chips, at elevated temperatures, with or without pressure, with solutions of sodium hydroxide, soda or neutral sulfite, followed by fiberizing in disk refiners, e.g., under pressure in the Asplund defibrator. The pulp thus

produced (chiefly out of waste materials and wood of poor quality) is a more coarse pulp, especially suited for the manufacture of insulating products, saturating felts and some wrapping.

A new method of producing strong pulps from hardwoods has recently been proposed by C. E. Libby and F. W. O'Neil (12), the so-called "chemi-groundwood" process, which consists of a mild chemical treatment of the wood in block form, followed by mechanical defibering in a pulp grinder. The pulps thus manufactured—in a yield of 85-90 percent—are reported to be 3-4 times as strong as ordinary spruce groundwood.

The production of semichemical pulps has increased in the U.S. during the last few years and amounted, in 1948, to approximately 800,000 tons (production from straw, bagasse, etc. excluded).

The resulting pulps from the various methods of semichemical pulping show a somewhat different composition if compared at the same yields (13). For example, increasing lignin contents and decreasing hemicellulose contents will be found in a comparison of acid sulfite, neutral sulfite, sulfate, soda and soda ash semichemical pulps. The alkaline reagents will naturally remove more extractives than the others. The degradation of cellulose is said to be greatest in soda pulping and least in neutral sulfite pulping. The acid and neutral sulfite pulps are brighter than the alkaline pulps. In this connection it may be mentioned that certain woods such as Black cherry and Scotch pine, which cannot be pulped with acid sulfite are easily reduced to pulp with neutral or alkaline cooking methods.

The outstanding characteristic of the hardwood semichemical pulps is their strength, which is much higher than would be expected from their short fiber length and often is equal to the strength of the same kinds of pulp from softwoods. The usefulness of semichemical pulps from several hardwoods is limited because of their low brightness.

Some hardwoods, such as aspen, birch and maple, used in newsprint manufacture give papers which are stronger than ordinary. Difficulties might arise, however, in modern fast-moving paper-machines, since the pulps often tend to be slow and to have low wet-web strength (14). Pulps from woods of light color, if mixed with groundwood or soda pulp, yield papers suitable for newsprint, and the tendency of the pure pulps—especially neutral sulfite semichemical pulp—toward being hard, sticky and transparent is, to some extent, counteracted. The stiffness of the semichemical fiber is, on the other hand, a desirable property in the production of, e.g., wound tubes, laminated solid paperboards and corrugating containers.

The above-mentioned limitations of hardwood semichemical pulps have made the problem of their bleaching especially important. Much research

has been done, chiefly by F. A. Simmonds and R. M. Kingsbury (15), on the use of the usual bleaching agents as well as sodium peroxide. Using a chlorine-hypochlorite multi-stage bleaching procedure, as much as 55-62 per cent of bleached pulp (based on the original oven-dry wood-weight) can be obtained. The strength properties of the pulps are considerably increased and are often equal to those of bleached softwood sulfites (see Table). Alkaline treatment following the chlorine can be used to alter the paper-making characteristics in the desired direction (16).

Neutral sulfite semichemical pulps are preferred for bleaching as they yield the strongest pulps at the lowest bleach consumption. For proper balance between yield and chlorine consumption the pulps should be cooked to about 10 percent lignin content. Because of their high content of wood polyoses, bleached hardwood semichemical pulps are easily beaten and therefore well-suited for greaseproof and glassine paper (17).

Table extracted from the paper by F. A. Simmonds and R. M. Kingsbury (15)

Species		Brightness G. I. %	Yield basis unbleached pulp	Yield basis wood %	Lignin	Strength properties at 550 ml. Schopper- Riegler freeness ¹			
						Burst, pls. per lb. per ream	Tear g. per lb. per ream	Tensile lb. per in. width	Number of double folds
Aspen (<i>Populus tremu- loides</i>)	unbleached	40.4	—	71.0	9.8	0.88	0.75	31.6	221
Neutral sulfite semi- chemical	bleached	81.0	84.5	60.0	0.3	1.30	1.19	37.9	488
Aspen	unbleached	13.4	—	76.0	17.3	0.68	0.84	24.7	59
Kraft semichemical	bleached	80.0	74.0	56.0	0.0	1.12	0.92	32.8	503
Black Tupelo (<i>Nyssa silvatica</i>)	unbleached	54.6	—	80.0	18.5	0.55	1.15	19.4	53
Neutral sulfite semi- chemical	bleached	82.0	68.0	54.4	—	1.09	1.42	32.9	569
Paper birch (<i>Betula papyrifera</i>)	unbleached	49.3	—	75.2	12.7	² 0.93	² 0.80	² 32.5	² 227
Neutral sulfite semi- chemical	bleached	78.5	74.4	56.0	1.4	² 1.16	² 0.92	² 37.6	² 68.5
Commercial Softwood Mitscherlich Sulfite	bleached	72.0	—	—	—	1.16	0.76	36.3	600
Shortleaf Pine (<i>Pinus echinata</i>)	unbleached	26.5	—	70.0	11.2	1.02	1.42	29.5	407
Neutral sulfite semi- chemical	bleached	80.0	—	—	0.0	1.33	1.55	31.3	983

¹ Ream weight 55 lbs.

² 400 ml. freeness.

II. Pulping with Chlorine and Alkali

Many methods of isolating plant fibers of various origins have been worked out (18) on the basis of the long-known ability of lignin to combine readily with chlorine to form water- or alkali-soluble compounds. It is common knowledge that Cross and Bevan were the first to study this reaction closely. Later work has proceeded along two lines; the use of chlorine water (DeVains) and that of chlorine gas (Cataldi-Pomilio). Since chlorine has very little penetrating action on wood, the latter must be pretreated with alkali before the chlorination can proceed. In order to facilitate the penetration of the chlorine, the wood is reduced to very small pieces. Thorough chlorination can also be achieved by reaction with chlorine under pressure, or by very long continued action of chlorine. When the chlorination is finished, the chlorinated material is washed out with water, alkali, or sodium sulfite. It is often necessary to repeat the chlorination and alkali treatment several times.

Adoption of the process in practical operation is determined by the cost involved in the consumption of chlorine and alkali (19). It has proved important to work out a continuous process. U. Pomilio (20) has succeeded in doing this. A number of plants employing his system for the utilization of straw, have been put into operation in the last ten years in various parts of the world. This is the only raw material utilized so far.

The Pomilio process is characterized by the following three procedures. The plant fibers are first treated with 1% sodium hydroxide at about 90°C., and then washed and pressed. Chlorination of the porous mass follows, and finally, after a water wash, the chlorinated material is extracted with dilute sodium hydroxide. The rentability of the process depends greatly upon the production of chlorine and sodium hydroxide at the plant. The plants constructed so far employ Giordani-Pomilio cells for this purpose. It is possible to arrange the process so that chlorine and caustic soda are consumed in the pulping in the same proportions in which they are obtained by electrolysis. The following figures may be quoted for this consumption in the pulping of wheat straw: 13 lb. sodium hydroxide and 25 lb. chlorine per 100 lb. 88% pulp from wheat straw (unbleached). The yield of pulp was 45%. An additional 2-3 lb. of chlorine is required for the bleaching.

G. Jayme (21) found that pulp of great strength can be obtained in large quantities from straw if the material is bleached with sodium chlorite after the alkali pulping. American workers had recommended sodium chlorite bleaching even earlier, particularly for the last of the several steps in the bleaching process for sulfate kraft pulp. The reason given was

that the color of the pulp could be improved without impairing the strength, even at very high temperature (22).

The high cost of sodium chlorite makes it impossible to pulp wood directly with chlorite. A. W. Sohn and F. Reiff (23) found that the direct production of sodium chlorite pulp required an amount of anhydrous sodium chlorite equal to not less than 75-125% of the weight of the wood. The yield of pulp from pine was at best 58%, or about the same as in the production of Cross-Bevan cellulose. The pulp must contain large quantities of wood polyoses, since the true cellulose content is about 40%. The average degree of polymerization was not less than about 1,300.

III. Pulping with Nitric Acid

Attempts were made quite some time ago to dissolve the lignins by the action of nitric or nitrous acids, and thus to obtain cellulose. G. J. Mulder (24) used fuming nitric acid for this purpose. A nitration of the cellulose did not occur; instead, the cellulose was largely transformed into hydrocellulose, as was proved by B. Tollens and R. W. Tromp de Haas (25). Since then, several investigators have described or patented procedures in which more or less concentrated nitric or nitrous acids were used (26). C. F. Cross and E. J. Bevan (27) found that it was not at all necessary to use strong nitric acid. Even dilute acid (4-7%) dissolved the lignin just as easily. They observed the formation of hydrogen cyanide during the process.

P. Kraus (28) in particular has investigated this problem. He used 3-4% nitric acid, acting preferably on straw and reeds. However, wood could also be completely pulped if it were cut fine enough. The acid consumption amounted to 0.5 to 1 lb. per pound of cellulose.

Kraus called attention to the fact that the pulping with nitric acid could not be carried out technically until a container sufficiently resistant to nitric acid came on the market. Krupp with his V2A steel provided a material which made the construction of such apparatus possible.

O. Routala and J. Sevón (29) soaked the wood with a solution of saltpeter, and then added an equivalent amount of sulfuric acid. The pulping was carried out at 75-95°C. and was finished after 18 hours. After the digestion, the residue was treated with alkali, which dissolved most of the lignin. The quality of the "saltpeter pulp" is said to be equal to that of sulfite pulp. Complete pulping requires a quantity of saltpeter equal to 35-40% of the weight of the air-dried wood.

J. Shimoda (30) has also investigated this problem. He treated Japanese pine with nitrogen dioxide for 1½-4 hours at 60-97°C. Afterwards the

mass was washed out with dilute sodium hydroxide. Shimoda succeeded in obtaining relatively good pulp, which had high content of α -cellulose.

The chemists at the I. G. Farbenindustrie have succeeded (31) in producing nitric acid pulp commercially. Beech wood has been used for this purpose at the plant at Wolfen. The procedure is practicable only when cheap waste nitric acid is available.

This pulp can be prepared with a content of 98% α -cellulose. Such high-grade cellulose corresponds chemically to cotton linters, and can be used in the cuprammonium as well as in the acetate process for rayon.

REFERENCES

1. Tilghman, B. C., U. S. Pat. 70,485 (Nov. 5th, 1867).
2. Mitscherlich, A., German Pat. 2,939 (1874); see also *The Engineer* 18 sept. 1874, p. 227.
3. Schwalbe, C. G., and Hagström, N. F., *Cellulosechemie* **11**, 233 (1930).
4. Schwalbe, C. G., German Pat. 282,050 (1913); *Hauptversammlungsber. Ver. Zellstoff-Papierchemiker Ingenieure* **1917**, p. 46.
5. Cross, C. F., British Pat. 4,984 (1880).
6. McKeefe, E. P. and Bradley, L., German Pat. 375,053 (1923); Canadian Pat. 219,557 (1922); *Paper Trade J.* **88**, No. 7, 131 (1929); Clark, J. d'A., *ibid.* **83**, No. 22, 13 (1926); Drewsen, V., *ibid.* **83**, No. 24, 41 (1926); Hausen, J., *ibid.* **84**, No. 9, 56 (1927); for bibliography, cf. Rue, J. D., *ibid.* **81**, No. 16, 54 (1925).
7. Cf. Drewsen, V., see Ref. 6.
8. Clark, J. d'A., see ref. 6; Schacht, W., German Pat. 122,171 (1900); cf. also Cobley, T. H., German Pat. 21,268 (1882).
9. Rue, J. D., Wells, S. D., Rawling, F. G., and Staidl, J. A., *Paper Trade J.* **83**, No. 13, 50 (1926); Rawling, F. G., and Staidl, J. A., *ibid.* **81**, No. 8, 42 (1925); Curran, C. E., *ibid.* **88**, No. 5, 66 (1929); Bray, M. W., and Eastwood, P. R., *ibid.* **90**, No. 25, 57 (1930); *ibid.* **93**, No. 17, 38 (1931); Chidester, G. H., and McGovern, J. N., *Tech. Assoc. Papers* **22**, 545 (1939); McGovern, J. N., Evert, J. N., Chidester, G. H., *Paper Trade J.* **113**, No. 23, 27 (1941); Peterson, H. E., Bray, M. W., and Ritter, G. J., *ibid.* **121**, No. 2, 37 (1945); Aries, R., *ibid.* **128**, No. 1, 21 (1949); Keller, E. L., and McGovern, J. N., *Tappi* **32**, No. 9, 400 (1949); Chidester, G. H., *Paper Trade J.* **129**, No. 21, 84 (1949).
10. Heritage, C. C., Curran, C. E., Monsson, W. H., Chidester, C. H., *Paper Trade J.* **87**, No. 17, 129 (1928); Curran, C. E., Monsson, W. H., Chidester, G. H., *ibid.* **90**, No. 14, 65 (1930); Rowley, H. J., *Pulp Paper Mag. Can.* **38**, 92 (1937); Sutherland, D. G., *Paper Trade J.* **124**, No. 22, 62 (1947); Jayme, G., and Lochmüller-Kerler, E., *Holz Roh- u. Werkstoff* **5**, No. 1, 10 (1942); Bray, M. W., and Martin, J. S., *Tech. Assoc. Papers* **27**, 224 (1944); Jennes, L. C., and Nystrom, G. L., *Paper Trade J.* **126**, No. 24, 53 (1948); Chidester, G. H., see Ref. 9.
11. Asplund, A., *Wochbl. Papierfabr.* **71**, No. 45, 590; No. 46, 607; (1940); *Chem. Abstracts* **35**, 4200 (1941); Lundberg, A. H., *Pacific Pulp Paper Ind.* **15**, No. 6, 16 (1941); Nickerson, A. W., *Tech. Assoc. Papers* **24**, 461 (1941); Ritter, G. A., *Pulp Paper Mag. Can.* **46**, 528 (1945); *Pulp and Paper* **22**, No. 8, 44 (1948).

12. Libby, C. E., and O'Neil, F. W., *Tappi* **4**, 161 (1950).
13. Chidester, G. H., see Ref. 9.
14. McGovern, J. N., *Tech. Assoc. Papers* **29**, 473 (1946); see also *TAPPI Bulletin* No. 53, May 31 (1945); *Northeastern Wood Utilization Council*, New Haven, Bulletin No. 14 (1947).
15. Simmonds, F. A., and Kingsbury, R. M., *Paper Trade J.* **124**, No. 4, 53 (1947); Kingsbury, R. M., Simmonds, F. A., Mills, R. T., Fennel, F. L., *ibid.* **123**, No. 11, 50 (1946); consult original for further references; cf. McGovern, J. N., Schafer, E. R., and Martin, J. S., *TAPPI Monograph* No. 4, 130 (1947).
16. Murdock, H. R., *Paper Trade J.* **124**, No. 4, 51 (1947); Peterson, H. E., Bray, M. W., and Ritter, G. J., see Ref. 9.
17. Fries, K. W., *Paper Trade J.* **122**, No. 21, 43 (1946).
18. Cf., for example, Menzies, R. C., and Davies, A. E., British Pat. 1,476 (1872); Green, H., U. S. Pat. 1,206,777 (1916); Cataldi, P., British Pat. 101,475 (1916); Waentig, P., German Pat. 349,842 (1917); Franz, A., German Pat. 323,936 (1919); Vains, A. R. de, British Pat. 189,561 (1921), 198,975 (1922); Pomilio, U., *Chimie & Industrie* **6**, 267 (1921).
19. Cf. Wenzl, H., *Papier-Fabr.* **24**, 809 (1926).
20. Cf. Waentig, P., *Zellstoff u. Papier* **17**, 352, 392 (1937).
21. Jayme, G., *Cellulosechemie* **20**, 43 (1942).
22. Cf., for example, Taylor, M. C., White, J. F., Vincent, G. P., and Cunningham, G. M., *Ind. Eng. Chem.* **32**, 899 (1940); White, J. F., and Vincent, G. P., *Paper Trade J.* **111**, No. 12, 39 (1940); Wenzl, H., *Papier-Fabr.* **39**, 177 (1941).
23. Sohn, A. W., and Reiff, F., *Papier-Fabr.* **40**, 1 (1942).
24. Mulder, G. J., *J. prakt. Chem.* [1] **39**, 152 (1846); cf. also Sacc, F., *Ann. Chim. Phys.* [3] **25**, 218 (1849).
25. Tollens, B., and Tromp de Haas, R. W., *Ann.* **286**, 296 (1895).
26. Barre, C. H., and Blondel, C. M., *Dinglers Polytech. J.* **164**, 464 (1862); Lifschütz, J., *Ber.* **24**, 1188 (1891); Schwalbe, C. G., German Pat. 204,460 (1907); Müller, R., German Pat. 339,303 (1918).
27. Cross, C. F., and Bevan, F. J., *Ber.* **24**, 1772 (1891).
28. Kraus, P., *Papier-fabr.* **23**, 797 (1925); German Pat. 391,713 (1922), 395,191 (1923), 395,192 (1923); see also *Papier-Fabr. Fest- u. Auslandsheft*, **71**, 3 (1931).
29. Routala, O., and Sevón, J., *Cellulosechemie* **7**, 113 (1926).
30. Shimoda, J., *Cellulose Ind. (Tokyo)* **12**, 3, 13 (1936); *Papier-Fabr.* **34**, 137 (1936).
31. Cf. Feldtmann, G. A., *Zellstoff u. Papier* **13**, 55 (1938). On the analysis of the waste liquors from nitric acid pulping, cf. Whittemore, E. R., Reid, J. D., and Lynch, D. F. J., *Ind. Eng. Chem.* **30**, 1192 (1938); Malcolm, A. M., "Pulping of Beechwood with nitric acid at Wolfen near Leipzig", P. B. 18,906; see also P. B. 52,008, 41-53 (1940).

CHAPTER VIII

DELIGNIFICATION WITH BLEACHING AGENTS

By HANS WILHELM GIERTZ¹

Technical pulps prepared by either the sulfite or the sulfate process still contain some residual lignin, in amounts which vary with the quality of the pulp. A study of the course of the pulping process reveals that the dissolving of the lignin becomes relatively slow at the end of the cook. The lignin content of paper pulp varies between 1.5 and 6%, and that of unbleached rayon pulp from 0.5 to 1.5%.

If pulps are to be prepared which are both lignin-free and very white, the residual lignin must be removed by means of reagents other than cooking liquors. In practice, this is accomplished by treatment with chlorine or certain chlorine compounds.

The main object of bleaching is to remove the incrusting substances which cause discoloration, and thus obtain a pure white product. The colored impurities in sulfite pulp appear to consist entirely of lignin compounds (1, 2). The dark brown color of sulfate pulp may also be due to sulfur-containing lignin products formed during the cook, either by extensive condensation (3) or by degradation (4). It is possible, however, that the discoloring substances are also formed partly by humification of the carbohydrate constituents of the wood (cf. Chapter VI).

The bleaching process can best be regarded as a continued pulping in which it is a matter of converting the lignin products into water-soluble form. This process must be carried out as gently as possible, so that the carbohydrate is not attacked. If it were, the strength would be decreased in the case of paper pulp, while the rayon pulp would show irregular decreases in viscosity and in α -cellulose content. A prevailing tendency in the development of bleaching technique has therefore been either to adjust the bleaching conditions in such a way that the attack on the cellulose constituents is minimized, or to introduce new bleaching agents with such properties that only the lignin compounds, and if necessary other discolorizing incrustations, are attacked while the cellulosic material is left intact. The use of a preliminary bleaching by means of acidic chlorination followed by an alkaline extraction, and the introduction of buffered

¹ Research Associate, Swedish Forest Products Research Laboratory, Stockholm.

hypochlorite bleaching and final bleaching with the new bleaching agents sodium chlorite and chlorine dioxide are examples of this.

S. Samuelsen (5) has divided the course of bleaching into the following reactions:

- I. the dissolution of the incrustants
- II. the destruction of the colouring matters
- III. the oxidative breakdown of the incrustants after their having been set free from the cellulosic material—the further oxidation of the incrustants in solution, and
- IV. an oxidizing attack on the cellulosic material.

Available chlorine is consumed in all these reactions. The two first reactions are of value but the second two are undesirable and have to be decreased. In a one stage hypochlorite bleaching, all these reactions take place simultaneously, but they are to some extent separated from each other in a multi-stage treatment. The chlorination converts the lignin into products, some of which are soluble in the acid chlorine solution, while others dissolve only in the alkaline wash water. The hypochlorite treatment removes the remaining colored impurities. The undesirable oxidation reactions III and IV can be largely eliminated by carrying out the bleaching process in several chlorination and hypochlorite stages with intermediate alkali washes, which, above all, benefits the lignin dissolving reaction I.

The action of the chlorine may be described as follows. Chlorine can react with lignin either by substitution or by oxidation. The addition of chlorine is probably out of the question, since this would require the presence of double bonds in the lignin molecule (6, 7, 8). The relative extents of the substitution and oxidation reactions can be calculated from the quantity of hydrogen chloride formed; substitution yields one molecule of HCl per molecule of chlorine consumed, while oxidation yields two molecules of HCl per chlorine molecule.

Whether the chlorine reacts by substitution or oxidation is determined, to a certain extent, by the distribution of the active chlorine in the bleaching liquor among elementary chlorine, hypochlorous acid, and hypochlorite ion.

Chlorine hydrolyzes to give hydrogen chloride and hypochlorous acid, as follows:



and the hypochlorous acid is further dissociated into hypochlorite ions. These equilibria are rapidly attained. It follows, therefore, that the relative quantities of chlorine, hypochlorous acid, and hypochlorite ion are deter-

mined solely by the pH of the solution. In strongly acid solutions the active chlorine is mostly present as elementary chlorine; in slightly acid solutions hypochlorous acid predominates; alkaline solutions contain chiefly hypochlorite ions. The distribution is represented in Fig. 83.

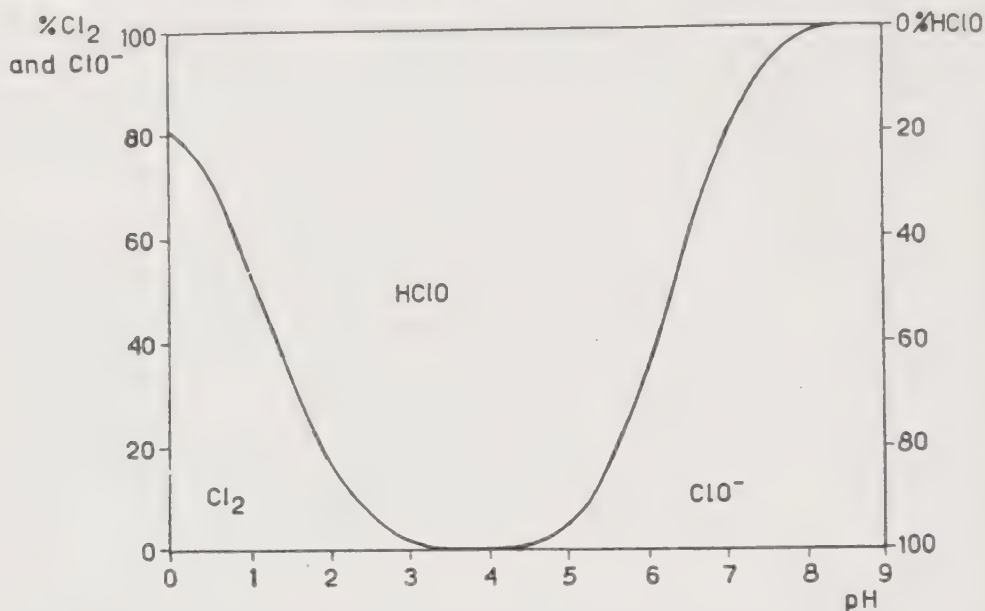


Fig. 83. The distribution of chlorine among elementary chlorine, hypochlorous acid, and hypochlorite ion in a 0.01 *N* solution of chlorine in water, at various pH's.

High chlorine concentrations cause the equilibrium to be shifted to the left i.e., in favor of elementary chlorine. High temperatures, on the other hand, cause a displacement in favor of the formation of hypochlorous acid.

I. Chlorination

The reaction between chlorine and unbleached pulp proceeds very rapidly at first, but the velocity of the reaction soon diminishes. This has been interpreted to mean that two reactions are taking place with different velocities; the more rapid reaction, which predominates in the early stages, is thought to be a substitution reaction, while the slower reaction is presumed to be an oxidation (9). A kinetic study by W. R. Carmody and J. S. Mears (10) has shown that this is indeed the case. Many investigations have also been carried out with the purpose of determining how much chlorine reacts by substitution, and how much by oxidation. As has been pointed out above, this can be calculated from the production of hydrogen chloride. It is found that 60-80% of the chlorine reacts by substitution, and the remainder by oxidation (7, 11, 12, 13).

This relationship is shown by an investigation of H. W. Giertz (2). Fig. 84 shows the course of the reaction when a sulfite pulp is chlorinated. Most of the chlorine is consumed in the first five minutes. The diagram also shows how the two separate reactions proceed, the substitution taking

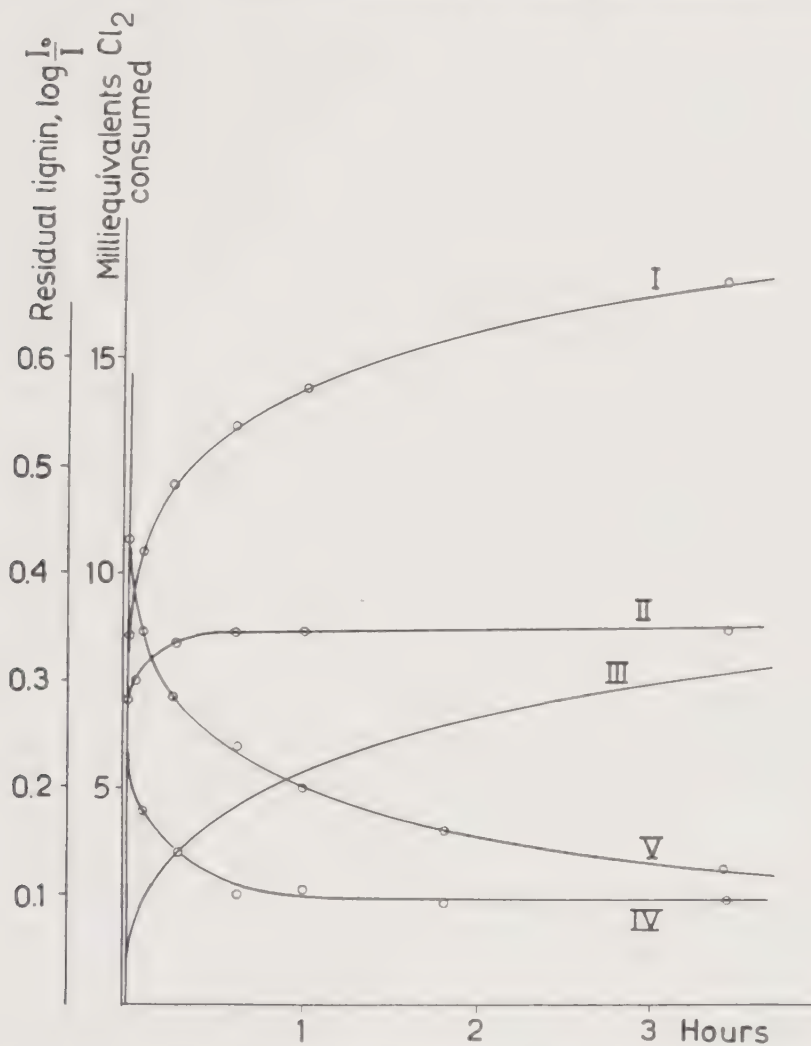


Fig. 84. The course of the chlorination of a sulfite pulp. The pulp is treated with an excess of chlorine and the chlorine consumption is determined after various times. The total consumption of chlorine (I) is divided into two parts, viz. (II) the substitution part, and (III) the oxidation part. The residual lignin in the pulp is estimated (IV) both after water-washing (V) and alkaline extraction (IV).

place with extreme rapidity, and being completed within 15 minutes. The oxidation proceeds with constant velocity throughout the treatment with chlorine, except at the very beginning; this indicates that certain groups in the lignin are particularly easily oxidized.

In this connection, the course of the removal of the lignin should also be noted. This was followed by determination of the residual lignin (14), both after washing with water, and after extraction with alkali. Part of the lignin is very rapidly converted into an alkali-soluble form. This fraction, which may be dissolved by alkali extraction, is alkali soluble after only 15 minutes chlorination time. The dissolution after the above period is of insignificant value. This course coincides with the substitution reaction. When the substitution reaction is complete, no more lignin can be extracted with alkali. If the chlorination reaction is allowed to continue a further amount of chlorine is consumed by oxidation and this consumption has no influence on lignin dissolution. If, however, after chlorination the pulp is washed only with water, the quantity of lignin dissolved is far less than with alkaline washing. This is particularly true in the early stages of chlorination. After a long chlorination time, when the lignin has been destroyed by the oxidation reaction, the lignin chlorides also become water-soluble. Giertz, therefore, concluded that during the chlorination of sulfite pulps the chlorinating effect of chlorine, in the proper sense, and not the oxidizing effect, is the decisive factor in the dissolution of the lignin.

E. Hägglund, H. W. Giertz, and B. Nelson (3) have demonstrated, however, that when sulfate pulps are chlorinated, oxidation is of some importance chiefly because of the highly condensed nature of the lignin in sulfate pulp. The optimum time for the dissolution of lignin is as much as 60-90 minutes, whereas sulfite pulps require chlorination for only 15-45 minutes, depending on the lignin content (2). E. Hägglund and H. Urban (15, 96) early called attention to the importance of oxidation in connection with the chlorination. According to these authors, the chlorination should be combined with a hypochlorite treatment, which may come either before or after the chlorination. This is in agreement with the results obtained in the commercial procedure proposed by J. R. MacMillan (16) and by E. B. F. Sunesson (17), in which the pulp is treated first with hypochlorite, and then with chlorine, or the reverse procedure of J. D. Rue and J. S. Sconce (18, 19), in which the pulp is chlorinated with an excess of chlorine, which is then converted to hypochlorite by the addition of lime. All of these procedures remove the lignin more effectively than the usual chlorination.

It has been emphasized above that the active chlorine in solution exists partly in the form of elementary chlorine, and partly in the form of hypochlorous acid. Of the two forms, the elementary chlorine acts by chlorination, and the hypochlorous acid primarily by oxidation (21, 22). Changes in the relative chlorinating and oxidizing powers of the solution

can be effected by altering the pH. An investigation of this point has been made by W. O. Hisey and C. M. Koon (23), who studied the bleaching action in solutions buffered at pH 0.8-12.5. It was determined that the reaction velocity was greatest in the strongly acid solutions, and decreased steadily as the pH was raised. According to Carmody and Mear's

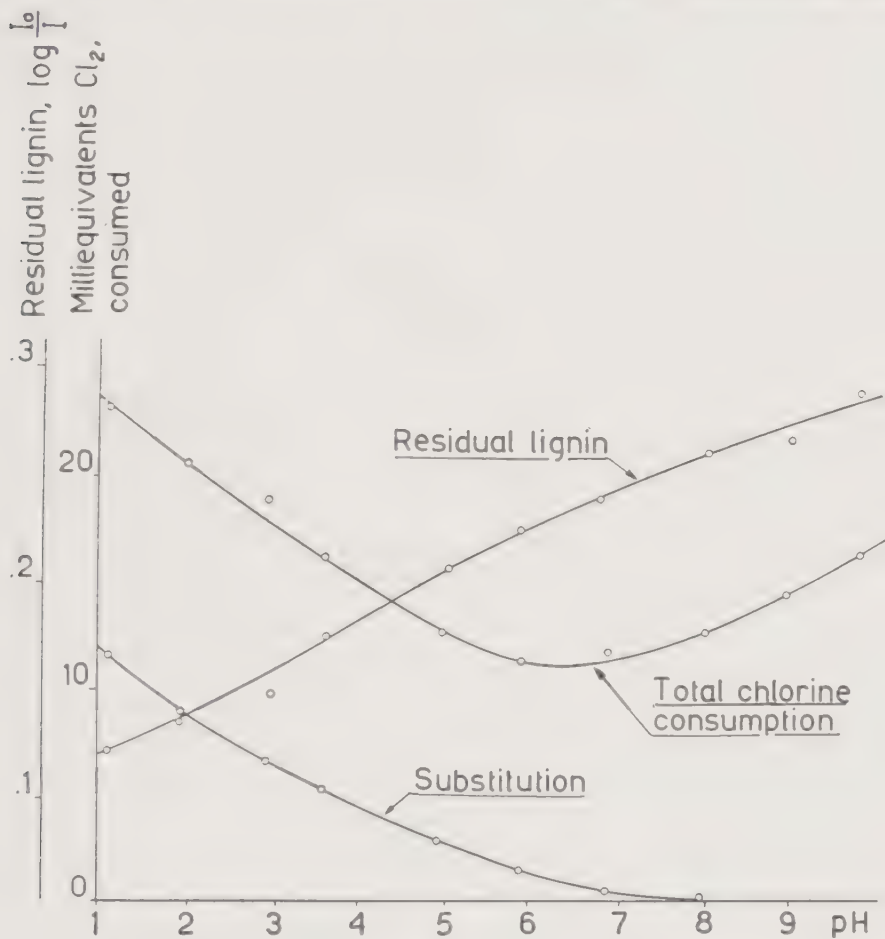


Fig. 85. Chlorination at varying pH. A sulfite pulp is treated for 1 hour with chlorine-water solutions buffered to certain pH's. The total chlorine consumption, the chlorine consumed by substitution, and the residual lignin content after alkaline extraction have been determined.

later calculations, the actual chlorination, accompanied by a certain amount of oxidation, takes place on the acid side. In the alkaline solutions the chlorine acts as oxidizing agent (10).

The influence of the pH of bleaching medium upon the dissolution of lignin is shown in Fig. 85. Pronounced chlorination takes place only in strongly acid solutions. The substitution reaction decreases progressively towards higher pH and the dissolving of lignin becomes poorer in the

same sequence. The oxidation reaction predominates during the alkaline bleaching i.e. in the usual hypochlorite process. The substitution ceases at pH 7 to 9, depending on the lignin content and the amount of chlorine employed (2). Since the chlorination is carried out commercially in unbuffered solutions, the formation of hydrochloric acid soon causes the pH to decrease to a value of about 2-1.6, depending on the chlorine consumption. Technical chlorination, therefore, takes place under conditions favorable for substitution. It has even been proposed to increase the acidity during the chlorination by addition of acid (10).

The temperature has only an insignificant effect on the progress of chlorination. At a higher temperature the chlorine is consumed more rapidly but the lignin dissolution is improved only very slightly (24, 25). The temperature in technical chlorination is therefore not controlled but varies with the season of the year (26).

By brominating in the presence of hydrogen bromide to repress the hydrolysis, K. Freudenberg and his co-workers (6) demonstrated that their lignin reacted entirely by substitution of bromine in the benzene nucleus. No addition took place. The methoxyl group was not removed by this bromination, but was split off in aqueous solution (13, 22, 27). It was later shown by W. Lautsch and G. Piazzolo (28) that the substitution takes place in para-position to the methoxyl group. The investigations of H. Hibbert and his co-workers (22) demonstrated that the uptake of chlorine occurs with simultaneous splitting of methoxyl. This splitting yields quinone or diketo groups, which are oxidized to carboxyl groups by the hypochlorous acid. The side chain of the lignin molecule is also probably chlorinated and oxidized at the same time. The acidic groups formed by these reactions make the lignin alkali-soluble; the solubility in the acid chlorinating fluid, however, is negligible. These facts are illustrated in the chlorination of a sulfate pulp which has been incompletely chlorinated. According to Hibbert, the chlorination and splitting of methoxyl takes place most easily in acid solution, less well in neutral solution, and only to a negligible extent in alkaline solution.

This chlorination accompanied by demethoxylation agrees with the rapid initial reaction known from technical chlorination. The slow oxidizing reaction has been shown, in experiments both with lignosulfonic acid in aqueous solution and with pulp in a heterogeneous system, to be of the second order. The reaction velocity in the chlorination is thus determined not by diffusion but by chemical factors.

L. L. Larson (13) found that some of the sulfonic groups of lignosulfonic acid were split off by chlorination. When large quantities of chlorine were

consumed, the extent of splitting increased. K. Kratzl and C. Bleckmann (29) observed complete splitting of the sulfonic acid group on bromination of liginosulfonic acid.

From the point of view of technical economy the question arises as to how much chlorine is reasonably necessary to be put in at the chlorination stage. The bleach-demand of the pulp is usually given in terms of the total quantity of chlorine, and the question is how to distribute this quantity between "chlorination" and "hypochlorite bleaching." It is commonly known that the pulp readily takes up chlorine to a certain extent. There are, however, different opinions as to whether this total amount is the

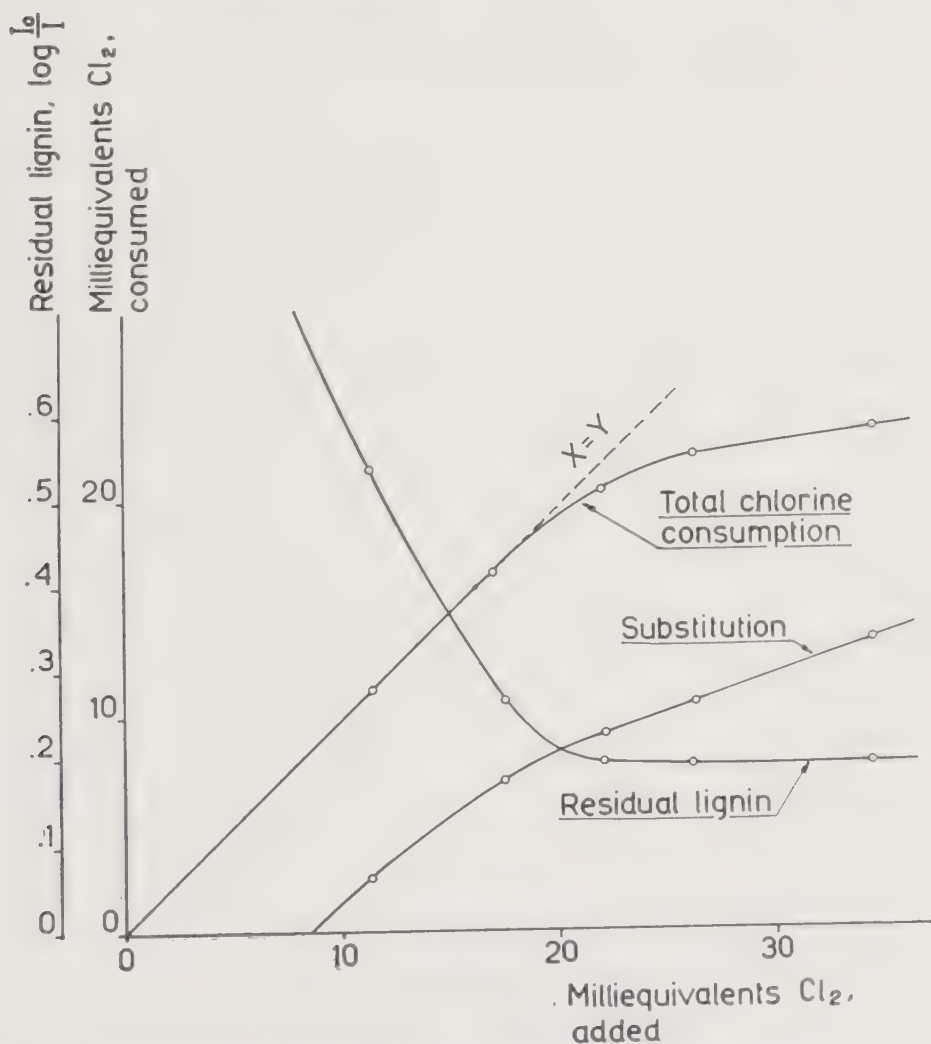


Fig. 86. Chlorination with varying amounts of chlorine. A sulfite pulp is treated for 1 hour and the residual lignin is estimated after alkaline extraction.

most suitable for the chlorination, or whether the input can be decreased or eventually has to be increased. The figures reported in the literature are rather divergent on this point, but indicate that 55-90% of the total chlorine should be in the form of elementary chlorine (7, 30, 12, 9, 31). S. Samuelsen (5) found for sulfite pulp, and F. Löschbrandt (32) for sulfate pulp, that the maximum whiteness was obtained when the chlorine was so distributed that the maximum possible solution of incrusting materials took place during the substitution. The quantity of chlorine required for the hypochlorite bleach was determined individually for each case.

With regard to the distribution between substitution and oxidation, the influence of the chlorine input on lignin dissolution is illustrated in Fig. 86. As long as the chlorine is completely consumed, more and more lignin is dissolved out in the subsequent alkali wash. When at a certain chlorine dosage the pulp ceases to absorb chlorine completely, the maximum lignin dissolution has been attained (2).

When small amounts of chlorine are used, it is completely consumed by oxidation alone (7). Substitution begins only when the chlorine has reached a certain concentration. After the optimum concentration for dissolution has been reached, most of the chlorine reacts by substitution. Further chlorination obviously affects only lignin which has already become soluble (32, 33).

When the chlorine requirements for optimum solution are determined in this way, it is found that unbleached sulfite pulp consumes 1.5 g. of chlorine per gram of lignin. Sulfate pulp requires somewhat more chlorine. These results are in fair agreement with the reports of other investigators (10, 22).

It is impossible to delignify the pulp quantitatively in a single chlorination operation. Even with an excess of chlorine the reaction with the lignin ceases before all of the lignin has been able to react. After an alkaline wash the pulp readily takes up chlorine again in a second chlorination. The chlorination reaction again proceeds rapidly but ceases before all residual lignin has been acted upon. The chlorination products must again be dissolved before it is possible to attack the residual lignin any further. This topochemical effect may be explained partly by the assumption that the chlorine molecules are unable to penetrate the native lignin or the superficial regions of chlorinated lignin which are formed during chlorination, and partly by the manner in which the lignin is enclosed in the fiber wall, i.e., by the morphological structure of the fiber (2). This effect is particularly evident during acidic reactions such as chlorination and chlorine dioxide bleaching. During hypochlorite bleaching the effect is not so pronounced because the reaction products are continuously dissolved in the alkaline medium.

For the same pulp this limit of delignification varies according to the chlorine activity. Thus, for example, the dissolution is better at lower pH. The chlorine activity is particularly high in chlorination with gaseous chlorine. Here the residual lignin content in the pulp is very low after the chlorination operation (2, 34).

The quantity of residual lignin in the pulp after chlorination followed by alkaline washing, is partly dependent upon the quantity of lignin in the unbleached pulp, and partly on the constitution of that lignin. The latter factor seems to be of an essential character with regard to sulfite pulp. If, for example, sulfite pulp is prepared in such a way that lignin condensation in the solid phase occurs, the pulp becomes more difficult to chlorinate than normal pulp with the same lignin content. The chlorine consumption is reduced, and it becomes harder to dissolve out the lignin. A high degree of whiteness can only be obtained by a hypochlorite bleach more strenuous than usual, and this results in greater damage to the carbohydrate (35). The following table gives typical figures for the quantity of residual lignin, both for pulps with various Roe numbers and for pulps cooked under various conditions. The pulps were prepared from Swedish spruce (*Picea exelsa*).

Cooking Conditions	Roe No.	Residual Lignin (1-4) After Chlorination and Alkali Wash
Cooking acid with 1.2% CaO and 5% SO ₂ .	7.8	0.58
Good impregnation. Maximum temperature 135° C.	4.2	0.24
	3.0	0.24
	1.8	0.19
	1.2	0.16
	0.6	0.13
a. Cooking acid as above, evacuation and impregnation 39 hrs. at 90° C, 3 hours to maximum temperature, 135° C.....	2.0	0.18
b. Cooking acid as above, impregnation 40 hrs. at 20° C, 8 hours to maximum temperature, 135° C.....	2.0	0.26
c. Cooking acid with 0.7% CaO and 5% SO ₂ , no special impregnation, 8 hours to maximum temperature, 135° C.....	2.0	0.40
Normal sulfate pulp.....	5.0	1.2

It is apparent that the residual lignin after chlorination is considerably greater in the case of sulfate pulp than in that of sulfite pulp. Häggglund's group has interpreted this to mean that the lignin becomes more extensively condensed during the sulfate cook. Variations in the conditions of cooking seems, however, not to be so important in the preparation of sulfate pulp as in that of sulfite pulp (36).

A two-stage chlorination of sulfite pulp is sometimes advisable, especially when it is important to minimize the attack on the pulp during the final bleaching. The two-stage chlorination is, however, particularly to be recommended for the bleaching of sulfate pulp, because the residual lignin content (12, 19, 33) is so high that the lignin can not be removed with hypochlorite without damaging the fibers. The repeated chlorination of sulfate pulp has been carefully studied by E. Hägglund and his co-workers (3). They found that while substitution was the predominate reaction during the first chlorination, just as much chlorine was consumed by oxidation as by substitution during the second chlorination. In further chlorinations the halogen reacted almost entirely by oxidation. According to these investigations, the lignin remaining in the fiber after the second chlorination is of such a character that it can not be removed by substitution with chlorine, but only by an oxidative degradation. There would be no theoretical justification for more than two chlorinations (3).

II. Alkali Washing

The chlorolignins formed during the chlorination are, as has already been pointed out, partly soluble in water and partly soluble in alkali. The relative amounts soluble in water and in alkali depend on the characteristics of the pulp itself. The idea is very widespread that the chlorolignins are, for the most part, soluble only in alkali. When sulfite pulps, however, have been sufficiently chlorinated, most of the lignin becomes water-soluble. N. W. Coster and R. I. Thieme (24) found, for example, that no less than 90% of the lignin was soluble in water. The same thing may be seen from Fig. 84 above. The water-solubility of the lignin of sulfate pulps is appreciably less, but even here at least half of the lignin will dissolve in water (3). If the pulp has been chlorinated incompletely, however, the chlorolignins are for the most part soluble only in alkali (22).

The dissolving out of the chlorolignins is mainly a physical process, in which the temperature and time of treatment are of the greatest importance.

F. Löschbrandt (32) found that the chlorolignins formed in sulfate pulps were not uniform in composition. The alkali extract could be divided into one fraction precipitable with acid, and another one which would not precipitate. The first fraction presumably consisted of lignin products of high molecular weight, which gave the alkali extract a dark color. The solubility in alkali is due to the large number of acid groups. The equivalent weight of this fraction was 130. The fraction which does not precipitate

with acid consists chiefly of wood polyoses, or of oxycellulose and lignin degradation products if the chlorination has been carried sufficiently far. According to Löschbrandt, there is a quantitative relationship between the amounts of the two fractions. He interprets this as meaning that the oxidative chlorination causes the splitting of a lignin-carbohydrate compound. This has also been pointed out by L. L. Larson (13). The dissolved lignin compounds may be present in the form of polybasic acids of high molecular weight (32). The solubility increases steadily with the alkalinity, up to pH 9-10. At still higher pH, the solubility increases only negligibly. The quantity of alkali required to reach a given pH depends upon the quality of the pulp. When the pulp is neutralized, only a small part of the alkali is consumed by the chlorolignins (37). An additional part of the alkali is taken up by the hydrochloric acid. Well-washed sulfite pulps consume about 0.5-1% of their weight in alkali, and sulfate pulps 1.5-2.5% (2, 3, 38). The washing can be carried out with various kinds of alkalies.

G. C. Arnold, F. A. Simmonds, and C. E. Curran (37) state that the dissolving power of sodium hydroxide, sodium carbonate, and sodium silicate are all approximately equal, when the same number of equivalents of alkali are used. Poorer solution is obtained with calcium hydroxide, because of the formation of difficultly soluble complexes (25). F. Hedborg has confirmed this fact in the case of the bleaching of sulfate pulps. He also found that the solubility in lime water decreased with increasing temperature. The solubility with ammonia was also less than that with sodium hydroxide (38).

The rate of solution, and hence of alkali consumption, is very rapid at first (39). This is probably due to topochemical reactions on the surface of the fibers (32). The time required for optimum removal of the soluble material is dependent on the temperature, but H. W. Giertz (2) found that the total amount of material which can be dissolved seems to be independent of the temperature, in the case of sulfite pulps. The same degree of delignification was obtained in 2 hours at 80° C as in 5 hours at 50° C, or in 10 hours at 20° C. F. Löschbrandt observed, however, that the temperature did affect the results he obtained with sulfate pulps. The dissolution increases markedly with the temperature, but is, regardless of the temperature, practically finished within 30 minutes (32). It has been found, however, that it is beneficial to extend the washing time further, because the quantity of lignin dissolved in the extra time is still appreciable in comparison to the lignin remaining in the pulp (3). Extending the alkali treatment from 30 to 90 minutes, for example, decreased the residual lignin by approximately 10%. In the bleaching of sulfate pulp,

therefore, it is expedient to wash with alkali at a temperature above 60°C for a relatively long time (3, 38). F. Löschbrandt reported that when the temperature reaches 70°C, a very large amount of hemicellulose is dissolved (32). The treatment with alkali is usually carried out at high pulp concentrations (14-18 %) in order to conserve heat. Consequently, the concentration of alkali in the liquor is relatively high; this accelerates the penetration of the fiber and favors the extraction.

Thorough washing with alkali is important in the bleaching process, particularly in the bleaching of sulfate pulps. Insufficient dissolution of the soluble lignin not only results in increased chlorine consumption in the subsequent steps of the process, but also makes additional treatments necessary at times in order to obtain the desired degree of whiteness. Because of the topochemical character of the bleaching reaction, it is impossible to cause the reaction with chlorine or hypochlorite to go as far after an incomplete washing as after an effective one. The historical development of the bleaching process reveals, therefore, that more and more importance has been assigned to the alkali washing. The latter is sometimes accompanied by a wash with hot or cold water (40, 41). The alkali wash can be made more effective by the addition of small quantities of sodium metaphosphate (42, 43).

III. Hypochlorite Bleaching

Hypochlorite bleaching is also a topochemical reaction. The velocity of the reaction is great at first, but decreases before all the lignin has reacted (44). The reaction products are, however, soluble in alkali, and are therefore continuously removed. The bleaching agent, therefore, continually comes in contact with unreacted lignin, and if the treatment is continued for a long enough time a fiber completely free of lignin is finally obtained.

There has been considerable question as to what constituent of the hypochlorite solution is effective in the bleaching. It could be either the hypochlorite ion, or the undissociated hypochlorous acid, or both. All three of these possibilities have had their advocates (45). The well-known fact that the bleaching proceeds more easily as the alkalinity decreases, while at the same time, the attack on the cellulose increases, is explicable on the basis of the assumption that hypochlorous acid is the oxidizing agent in the bleaching liquor, as it is in pure hypochlorite solutions. One would then suppose that the attack on the cellulose would be greatest when the concentration of hypochlorous acid is at a maximum, i.e., at pH 4-5 (cf. Fig. 83). This is not the case, however. The cellulose is most attacked at pH 6.5-7.5. H. Kauffmann (46) assumes that the oxidizing agent is a

complex of hypochlorous acid with hypochlorite ion, and that the maximum formation of the complex takes place in neutral or slightly alkaline solution. J. J. Weiss (47), on the other hand, is of the opinion that the oxidation depends upon two factors—the action of the hypochlorous acid, and the diffusion inside the fibers. The diffusion is aided by swelling, and the extent of swelling increases with the pH of the bleaching liquor. A combination of these two factors, both of which are influenced by the pH, but in opposite directions, would lead to optimum conditions in an approximately neutral solution (48). The ideas of both Kaufmann and Weiss have not, however, been confirmed experimentally, and the question is therefore still open.

It has been emphasized above that oxidation is the primary reaction during the bleaching with hypochlorite. When hypochlorite acts directly on unbleached pulps in only slightly alkaline solutions, a certain amount of substitution may also occur. (11, 49). However, when hypochlorite is used to finish the bleach, it probably acts only by oxidation. The lignin products are degraded to colorless acids which form water-soluble salts with alkali. After these acids have been dissolved they are, to a large extent, further oxidized to carbon dioxide (50).

From a practical standpoint, the reaction of the hypochlorite with the residual lignin is not as interesting as its reaction with the carbohydrates of the pulp. If the action of the hypochlorite is prolonged, the fibers may be appreciably attacked, if proper counter-measures are not taken.

When cellulose is oxidized, the most important reaction is the conversion of certain hydroxyl groups first to carbonyl groups, and then, if the conditions are favorable, to carboxyl radicals. Various kinds of oxycelluloses are formed, depending upon whether the primary hydroxyl in the 6-position, or the secondary hydroxyls in the 2- and 3-positions are oxidized (cf. p. 83). It is generally assumed that the primary hydroxyl groups are attacked by the usual oxidizing agents, including hypochlorite (51), but it is rather uncertain whether or not the secondary hydroxyl groups are oxidized. Periodic acid, meta-periodate and lead tetraacetate bring about a splitting of the linkage between the carbon atoms in 2- and 3-positions which results in the formation of a dialdehyde (52). Calculations by L. J. Heidt, E. K. Gladding, and C. B. Purves (53) indicate that the oxidizing agent effecting this glycol cleavage would have to satisfy certain requirements with respect to interatomic distances, valences, and oxidation potential, and that hypochlorous acid does not meet these requirements. It has actually been demonstrated that hypochlorite and hypobromite do not give the dialdehyde type of oxycellulose (52).

The carbonyl group first formed by the oxidation makes the cellulose chain unstable. The glucosidic linkages, which are usually alkali-stable, are then split by alkalies. According to E. Pacsu (54), who has studied the reaction in periodate-oxidized cellulose, the glucosidic linkage is weakened by enolization of the carbonyl group on the second carbon atom. Theoretically, the same could apply to oxycelluloses with an aldehyde group on the sixth carbon (55), or with keto groups on the second and third carbons. If the carbonyl groups are further oxidized to carboxyls, the cellulose chain is stabilized, so that it is not split by alkali (55, 56).

The pH of the bleaching liquor determines whether the hypochlorite oxidizes the hydroxyl groups mainly to carbonyl or to carboxyl groups. These two types of oxycelluloses give the pulp quite different properties. In alkaline solution carbonyl groups are formed first and are later oxidized to carboxyls. The copper number therefore rises at first, and later declines. The copper number rises again during over-bleaching (57). The absorption of methylene blue increases during the entire bleaching process (58). The oxycelluloses thus formed may be designated as *acid*, and are distinguished by their ability (after cation exchange) to bind metal ions and positive dyes. In acid solution the oxidation occurring gives mainly carbonyl groups. The copper number increases continuously, and the oxycellulose is designated as *reducing* (58).

A certain amount of attack on the cellulose chain always occurs during hypochlorite bleaching, no matter what the pH. This is reflected in a gradual decrease in the degree of polymerization of the cellulose. The speed of the degradation, however, depends very much upon the pH of the solution. It is greatest in neutral solution, and decreases on both the acid and the alkaline sides of the neutral point (58). At the beginning of the bleach, the unbuffered solution is alkaline (pH \sim 9), but because of the formation of hydrogen chloride, carbon dioxide, and other acids, the pH decreases to 6-7 (21, 59). Under these conditions the bleaching proceeds rapidly, to be sure, but at a pH where the cellulose is easily attacked. E. Opfermann (60) has therefore proposed adding alkali at the beginning of the bleach, so that the liquor will remain alkaline throughout the process. The bleaching then proceeds more slowly, but the conditions for dissolving the lignin are better, as has been explained above. With "buffered bleaching", the oxidative degradation is repressed in favor of the dissolving of the lignin; and the bleaching is carried out under conditions which spare the cellulose. The use of buffered bleaches has now become quite general, and only in cases where a short bleaching time is required is the process carried out in neutral solution.

Bleaching can be carried out with either sodium or calcium hypochlorite. In unbuffered solution, sodium hypochlorite is more alkaline and hence attacks the cellulose less than calcium hypochlorite. At the same pH, however, no appreciable differences can be detected between sodium and calcium hypochlorites, except for the composition of the ash in the resulting pulp.

Raising the temperature increases the velocity of bleaching, and also the extent of the attack on the fibers. The chlorine consumption doubles with every 7.5° C rise in temperature (8). Bleaching is usually performed at 30-35° C, but temperatures as high as 60° C are sometimes employed, especially for rayon pulps.

The cellulose is best protected against hypochlorite by carrying the initial chlorination so far that the amount of hypochlorite required for completing the bleach is relatively small—not more than about 1% of active chlorine. If the afterbleach requires more hypochlorite, it is best carried out in two stages, in the first of which the concentration of pulp is high, the temperature low, and the time short, so that only the delignification reaction takes place. (8, 12, 26, 61). The reaction products are dissolved separately by means of alkaline washing.

When sulfate pulps are bleached, it is necessary to divide the hypochlorite treatment into two or even three steps, depending on the quality of pulp required and the method of carrying out the preliminary chlorination. If this is not done, the great strength which is characteristic of the unbleached pulp is lost (19, 62, 63, 64, 65).

After the hypochlorite treatment, the pulp is washed carefully with water, and often also with a very dilute SO_2 -solution. The latter removes traces of chlorine which may be present, and makes the pulp somewhat whiter and lower in ash (62, 66, 67).

IV. Bleaching with Chlorine Dioxide and Chlorites

The fundamental investigations of E. Schmidt (68) revealed that chlorine dioxide has special properties as a delignifying agent for wood which make it possible to obtain very high yields of lignin-free products. For this reason chlorine dioxide was early proposed as a bleaching agent (69). The technical application of this agent began only very recently, however, when its commercial preparation became possible (70, 71, 72). Chlorite solutions have the same action as chlorine dioxide. Sodium chlorite has been produced on a commercial scale since the middle thirties (73).

Bleaching with chlorine dioxide can be carried out in acid, alkaline, or neutral solutions. The entire oxidizing power of the chlorine dioxide is utilized in the acid bleach, the reduction proceeding to chloride ions (74), according to the reaction



Only one fifth of the potential oxidizing power is used in the alkaline bleach, where the chlorine dioxide is reduced only to chlorite (75)



This latter reaction proceeds very rapidly, and the bleaching action is very powerful. A high degree of whiteness is easily attained, but a certain amount of attack on the carbohydrate of the pulp also occurs. The chlorite formed can be used in a second stage for chlorite bleaching (75). When the solution is buffered at neutrality the bleaching effect is intermediate between the acid and alkaline bleaches. In unbuffered solutions the pH drops to about 4 because of the formation of hydrogen chloride and acid reaction products, and the course of the reaction most closely resembles that of the acid bleach (74).

According to H. W. Giertz, the reaction in the acid chlorine dioxide bleach, which has to be carried out at 40-80° C. is particularly rapid at first (74). After only a few minutes, most of the chlorine dioxide which can react with the pulp has already been consumed. A corresponding increase in the whiteness of the pulp does not occur simultaneously with this initial rapid reaction. The whiteness improves only gradually, as the reaction products are dissolved or further degraded to colorless products. This requires 3-4 hours of treatment.

Neutral and alkaline chlorite solutions are stable. In acid solution the weak acid HClO_2 is liberated (76) which decomposes to chlorine dioxide (74, 77)



According to J. F. White, M. C. Taylor, and G. P. Vincent, chlorine dioxide is evolved from a chlorite solution by oxidation—with hypochlorite, for example—or by the addition of certain reducing agents (77).

Chlorite solutions show bleaching action only under certain conditions. They have no such action in alkaline or neutral media. A chlorite solution must be "activated" before it shows any bleaching effect. This is done by acidifying it and raising the temperature, or by adding oxidizing or reducing agents. It has already been emphasized that such "activating" procedures cause chlorine dioxide to be formed from the chlorite.

In chlorite bleaching the liquor is brought to a pH between 3.5 and 5.5 by the addition of sulfuric or hydrochloric acid, or acid salts (78). The most suitable temperature for bleaching sulfite pulp is said to be 45° C., and for sulfate pulp 70-80° C. The bleach consumption is 0.5-1%, calculated as active chlorine. The acidity of chlorite bleaching solutions is so high that the ordinary bleaching equipment can not be used, because of the danger of corrosion. However, if the chlorite is "activated" with oxidizing agents, the bleaching can be carried out at pH 7-9, and at a lower temperature. The most suitable oxidizing agents are chlorine and hypochlorite (78, 79, 80, 81). These agents will, however, attack the cellulose to a certain extent although the attack is not as great as that by an ordinary hypochlorite bleach. When neutral chlorine dioxide is used as a bleach, the reduction of the chlorine dioxide stops at the chlorite (74) stage, and the use of a bleach consisting of a mixture of chlorine and chlorine dioxide has therefore been proposed (82); the chlorite formed would then be reoxidized to chlorine dioxide.

When acid chlorite is used as a bleach, the rapid reaction observed with chlorine dioxide does not occur. The chlorite is consumed only gradually, and the bleaching period must therefore be extended to 4-5 hours, before the maximum degree of whiteness is obtained (74). It has also been found that acid chlorite forms free chlorine dioxide, at a rate dependent on the pH of the solution. At high acidities, the chlorine dioxide is produced rapidly, but in weakly acid media it is formed so slowly that it is immediately consumed by the pulp.

The action of chlorine dioxide on organic compounds has been intensively studied by E. Schmidt (68, 83). He found that aromatic compounds are easily attacked. Phenol, cresols, and other phenol derivatives are rapidly attacked, yielding highly colored quinoid compounds as primary products. Further action completely decomposes the benzene nucleus to carbon dioxide, oxalic acid, maleic acid, formic acid, and possibly other compounds. On the other hand, chlorine dioxide does not react with alcohols or carbohydrates, and acts only very slowly on even so reactive an aldehyde as formaldehyde. These facts explain why chlorine dioxide is such a suitable bleaching agent for pulp.

Chlorite solutions do not show the same reactivity toward organic substances as does chlorine dioxide. According to H. W. Giertz (74), acid chlorite solutions do not react with phenol and cresols, and react only slowly with quinone-forming phenols or with such lignin-containing materials as sawdust and liginosulfonic acid. Acid chlorite solutions rapidly form chlorine dioxide in the presence of aldehydes, but not of

ketones (77). The reaction of formaldehyde and chlorite yields at first hypochlorous acid, which reacts with more chlorite to give chlorine dioxide. Glucose and other reducing sugars are oxidized to the corresponding aldonic acids (84). Aldehyde groups in the cellulose are oxidized to carboxyls. Chlorite bleaching therefore causes a stabilization of the reducing oxycellulose toward alkaline hydrolysis.

There has been some disagreement as to whether the chlorite or the chlorine dioxide is the oxidizing agent in chlorite bleaches. According to the work of J. F. White, M. C. Taylor and G. P. Vincent (77, 85), the rapid consumption of the bleaching agent in comparison to the slow evolution of chlorine dioxide from pure chlorite solutions shows that the chlorite, or more accurately, the chlorite ion, is the active agent. On the other hand, according to H. W. Giertz (74), the chlorite ion is completely inactive. The free chlorous acid first decomposes by side reactions (with carbohydrate, for example) to yield chlorine dioxide, which is the actual bleaching agent. This decomposition is accelerated by the intermediate products formed.

The similarity between the bleaching with chlorite and with chlorine dioxide is remarkable. In both cases the bleaching liquor after some time comes to contain both chlorite and chlorine dioxide, in a ratio depending upon the conditions of the bleaching. The quality of the bleached pulp is also the same in both cases (74).

Because of the relatively high cost of these bleaching agents, they can be used only for completing the bleaching. Their most important application, thus far, have been in the bleaching of sulfate pulp (3, 70, 86) which can not be bleached to a high degree of whiteness with hypochlorite alone without considerably impairing the strength of the pulp (3, 20).

V. Bleaching and Pulp Characteristics

The deleterious attack of the bleaching agent on the cellulose and other carbohydrates consists chiefly in a splitting of the molecules. The degree of polymerization of the cellulose is thereby decreased, and the polymolecularity increased. In the case of rayon pulps these changes are manifested by a decrease in viscosity, and a fall in the α -cellulose content. The splitting of the molecules has a considerable effect on the strength of paper pulps, even when it is limited in extent. The reason for this is not yet understood. It is possible that an attack on the low-polymerized wood polyoses in the amorphous regions of the cellulose, which undoubtedly have some cohesive power, is of decisive importance.

It is often suggested that the attack on the fibers increases toward the

end of the bleach, because the lignin, which has a "protective" action, has been dissolved out, and the cellulose has thus become exposed (7, 87). It must be admitted, however, that this point has not been demonstrated by systematic studies. Other interpretations are possible. It is also conceivable, for example, that degradation beyond a certain definite point might lead to a rapid decrease in strength, as is the case with high-polymeric substances (88).

It has been emphasized repeatedly that the attack on the cellulose depends on the bleaching agent, and on the conditions during the bleaching. The extent of attack has been correlated with the oxidation potential of the bleaching agent (53, 78, 86). The following table gives the "effective oxidation potentials" (53) of several systems which are used in commercial bleaching.

	pH	E (Volts)	Reference
$2\text{Cl}^- = \text{Cl}_2 + 2\text{e} \dots\dots\dots$	2	— 1.20	(23)
	5	— 1.09	(23)
$\text{Cl}^- + 2\text{OH}^- = \text{ClO}^- + \text{H}_2\text{O} + 2\text{e} \dots\dots\dots$	7	— 0.93	(23)
	10	— 0.70	(23)
$\text{ClO}_2^- = \text{ClO}_2 + \text{e} \dots\dots\dots$		— 0.95	(76)
$\text{Cl}^- + 2\text{H}_2\text{O} = \text{ClO}_2^- + 4\text{H}^+ + 4\text{e} \dots\dots\dots$		— 0.75	(76)

The oxidation potential is not, however, the decisive factor in determining the reaction velocity, even though it is true that the bleaching agent must have a certain oxidation potential in order to oxidize the hydroxyl groups of the cellulose. Cellulose is, for example, more slowly attacked in acid chlorine solutions than in neutral or alkaline hypochlorite, although the oxidation potential of chlorine solutions is higher at lower pH. In view of the fact that ionic reactions are not involved, but rather heterogeneous reactions between molecules, it would appear that the oxidation depends not as much upon the oxidation potentials as upon the specific reaction mechanisms. Such a conception is supported by the fact that chlorine dioxide is a particularly favorable agent because it specifically attacks lignin compounds but not carbohydrates.

The attack on the cellulose during chlorination is insignificant. The viscosity decreases somewhat because of oxidation (24, 25, 65, 89), and not because of acid hydrolysis (7, 12, 30). Even repeated chlorination or chlorination at elevated temperatures, causes only a slight attack on the cellulose, provided an excess of chlorine is not employed (2). H. W. Hisey and C. M. Koon (23) report that chlorination of sulfite pulp causes an increase in tearing strength and folding resistance, while the bursting strength remains unchanged. E. Hägglund and his co-workers have come to the same conclusion with regard to the chlorination of sulfate pulp (3).

The wood polyoses of pulp are not attacked. The pentosan content and the percentage of α -cellulose are not changed (89). According to F. Burgstaller and R. Sonderhoff, pulp is more difficult to size with resin after a two-stage bleaching with chlorine than after a single hypochlorite bleaching (90).

The effect of the alkali extraction depends entirely upon the temperature and the quantity of alkali employed. The usual neutralization at a temperature of about 50°C has no effect upon the properties of the pulp. The addition of strong alkali at temperatures above 70°C results in some purification, with the result that the tearing strength increases, and the folding resistance decreases (37). The pentosan content is decreased, and the percentage of α -cellulose increases somewhat. The opacity is also increased, and the ash content and copper number diminished.

As has been emphasized repeatedly, the cellulose is most strongly attacked by hypochlorite bleaching. All the strength properties suffer when the pulp is bleached to a high degree of whiteness. The extent of the attack is, however, very much dependent on the manner in which the bleaching is carried out. The least damage results at pH 8-9, when the additions of chlorine are small and the temperature is kept low. Overbleaching is reflected chiefly in the folding resistance and the tearing strength. The pulp also becomes easier to beat (59). Viscosity always decreases during hypochlorite bleaching. It is possible, however, to keep the α -cellulose content constant by carrying out the bleaching under mild conditions (91). The polymolecularity of the pulp increases (92).

The degree of whiteness obtained depends upon the manner of cooking the pulp and the way in which the initial bleach is carried out. It is always possible to obtain a high degree of whiteness in sulfite pulps by making the hypochlorite bleach drastic enough. Under conditions which spare the cellulose, the bleaching action may stop at a whiteness of only 86% GE. This occurs when the cooking is so carried out that the lignin partially condenses, or when the initial bleaching is not sufficiently effective. If the cooking and the initial bleaching have been carried out in a suitable manner, it is easy to obtain a whiteness of 89-91% GE (35).

The pulp tends to turn yellow due to the formation of oxycellulose during the hypochlorite bleach (93). This effect is especially noticeable in the bleaching of sulfite pulps with high contents of wood polyoses (94). The opacity is not affected.

Bleaching with chlorine dioxide and acid chlorite does not result in sufficient attack on the cellulose to affect the strength characteristics and the α -cellulose content (20, 95). The chlorine dioxide bleach causes the cuprammonium viscosity to decrease somewhat, but in the chlorite

bleach it may increase a bit on account of the stabilization caused by the oxidation of the carbonyl groups to carboxyls. Pulps bleached with chlorine dioxide or chlorite show a very high resistance to subsequent yellowing (85, 94).

The following table compares the bleaching of sulfite and sulfate pulps, by various procedures.

Treatment	Bright- ness % GE	pc- Value	Visco- sity cP	Tensile Strength m.	Burst Factor	Folding En- durance	Tear Factor
<i>Sulfite Pulp</i> , Roe No. 3.0							
Unbleached	—	—	225	9,500	68	3,100	75
1. Hypochlorite bleach	85.7	10.7	54	9,150	69	4,400	69
2. Hypochlorite bleach, alka- line extraction, hypochlorite bleach	87.7	7.3	43	9,000	68	3,800	64
3. Chlorination, alkaline extrac- tion, hypochlorite bleach	92.0	5.9	35	8,000	55	1,100	67
4. Chlorination, alkaline ex- traction, hypochlorite bleach, alkaline extraction, hypochlorite bleach	92.0	4.9	33	9,200	60	2,500	62
5. Chlorination, alkaline ex- traction, hypochlorite bleach, alkaline extraction, chlorine dioxide bleach	92.6	2.6	139	9,700	69	4,800	81
<i>Sulfate Pulp</i> , Roe No. 5.4							
Unbleached	—	—	120	11,500	84	7,200	118
1. Chlorination, alkaline ex- traction, hypochlorite bleach	80.4	6.2	17.5	11,100	79	5,400	92
2. Chlorination, alkaline ex- traction, chlorination, alka- line extraction, hypo- chlorite bleach	83.4	4.2	26.3	10,800	80	7,400	104
3. Chlorination, alkaline ex- traction, chlorination, alka- line extraction, hypo- chlorite bleach, alkaline ex- traction, chlorine dioxide bleach	86.8	2.5	42.6	11,400	87	9,000	111
4. Chlorination, alkaline ex- traction, hypochlorite bleach, alkaline extraction, chlorine dioxide bleach, al- kaline extraction, chlorine dioxide bleach	89.5	1.6	40.3	11,400	85	9,500	117

The strength figures are given according to the Swedish method CCA 17 [*Svensk Papperstidn.* 50, 250 (1947)]; the viscosity has been determined according to CCA 16 [*ibid.* 49, 148 (1946)]. The pc-values are a measure of the tendency of the pulp to turn yellow (94).

REFERENCES

1. Forni, P. A., *Paper Trade J.* **119**, No. 11, 112 (1944).
2. Giertz, H. W., *Svensk Papperstidn.* **46**, 152 (1943).
3. Hägglund, E., Giertz, H. W., and Nelson, B., Meddelande från Cellulosaindustriens Centrallaboratorium, Ser. B, No. 7 (1944). Partly related in *Svensk Papperstidn.* **47**, 226 (1944).
4. Schwartz, H., McCarthy, J. L., and Hibbert, H., *Paper Trade J.* **111**, No. 18, 30 (1940).
5. Samuelsen, S., *World's Paper Trade Rev.* **106**, 1284 (1936).
6. Freudenberg, K., Beltz, W., and Niemann, C., *Ber.* **62**, 1554 (1929).
7. Heiwinkel, H., and Hägglund, E., *Svensk Papperstidn.* **43**, 391 (1940).
8. Rue, J. D., *Trans. Electrochem. Soc.* **73**, 137 (1938).
9. Schmidt-Nielsen, S., *Papir-J.* **26**, 83 (1938).
10. Carmody, W. R., and Mears, J. S., *Paper Trade J.* **106**, No. 20, 38 (1938).
11. Fotiev, S. A., *Pulp & Paper Mag. Can.* **39**, 749 (1938).
12. Kraft, F., *Papier-Fabr.* **36**, 429 (1938).
13. Larson, L. L., *Paper Trade J.* **113**, No. 20, 25 (1941).
14. Giertz, H. W., *Svensk Papperstidn.* **48**, 485 (1945).
15. Hägglund, E., and Urban, H., *Acta Acad. Aboensis Math. et Phys.* **5**, 4 (1928).
16. MacMillan, J. R., U. S. Pat. 1,547,138 (1925).
17. Sunesson, E. B. F., U. S. Pat. 2,140,863 (1939).
18. Rue, J. D., and Sconce, J. S., *Paper Trade J.* **95**, No. 17, 54 (1932).
19. Rue, J. D., *Paper Trade J.* **104**, No. 25, 19 (1937).
20. Jayme, G., and Rothamel, L., *Cellulosechemie* **21**, 7 (1943).
21. Rue, J. D., *Paper Trade J.* **110**, No. 26, 98 (1940).
22. White, E. V., Swartz, J. N., Peniston, Q. P., Schwartz, H., McCarthy, J. L., and Hibbert, H., *Tech. Assoc. Papers* **24**, 179 (1941).
23. Hisey, W. O., and Koon, C. M., *Paper Trade J.* **103**, No. 6, 36 (1936).
24. Coster, N. W., and Thieme, R. I., *Tech. Assoc. Papers* **24**, 204 (1941).
25. Phelps, M. W., and Schuber, J., *Paper Trade J.* **106**, No. 8, 126 (1938).
26. Clark, T., *Pulp & Paper Mag. Can.* **46**, 599 (1945).
27. Brauns, F. E., *Paper Trade J.* **103**, No. 5, 36 (1936).
28. Lautsch, W., and Piazzolo, G., *Ber.* **73**, 317 (1940).
29. Kratzl, K., and Bleckmann, Chr., *Experientia* **2**, 24 (1946).
30. Hägglund, E., *Svensk Papperstidn.* **41**, 519 (1938).
31. Schultén, K. af, *Finnish Paper Timber J.* **19**, 426 (1937).
32. Löschbrandt, F., *Kamyr Nachr.* No. 2-4 (1939) or "Bleaching of Sulfate Pulp", Tappi Monograph, New York, 1941.
33. Sprout, O. S. Jr., and Toovey, T. W., *Paper Trade J.* **124**, No. 11, 45; No. 12, 55 (1947).
34. Campbell, J., and Rolleston, L. O., *Paper Trade J.* **105**, No. 18, 126 (1937).
35. Giertz, H. W., *Svensk Papperstidn.* **50**, No. 11B, Jubilee Vol. E. Hägglund, 94 (1947).
36. Sutermeister, E., *Paper Ind.* **17**, 834 (1936).
37. Arnold, G. C., Simmonds, F. A., and Curran, C. E., *Paper Trade J.* **107**, No. 10, 32 (1938).
38. Hedborg, F., *Svensk Papperstidn.* **46**, 381 (1943).
39. Schmidt, G. E., Shera, B. L., and Toovey, T. W., *Paper Trade J.* **106**, No. 19, 44 (1938).

40. Prelinger, H., *Paper Trade J.* **107**, No. 11, 81 (1938).
41. Smith, E. H., Moore, A. B. Jr., and Chesley, K. G., *Paper Trade J.* **112**, No. 20, 35 (1941).
42. Gibson, W. R., *Paper Trade J.* **114**, No. 20, 53 (1942).
43. Lang, E. R., and Laurin, E. T., *Paper Trade J.* **116**, No. 20, 33 (1943).
44. Parsons, J. L., and Jackson, D. T., *Paper Trade J.* **107**, No. 14, 37 (1938).
45. Opfermann, E., and Hochberger, E., *Die Bleiche des Zellstoffs*, Berlin, 1935-1936, part I, p. 213.
46. Kauffmann, H., *Papier-Fabr.* **28**, 557 (1930).
47. Weiss, J. J., *Z. angew. Chem.* **44**, 488 (1931).
48. Opfermann, E., and Hochberger, E., *Die Bleiche des Zellstoffs*, Berlin, 1935-1936, part II, p. 89.
49. Opfermann, E., and Hochberger, E., *Die Bleiche des Zellstoffs*, Berlin, 1935-1936, part I, p. 218.
50. Rashback, H., and Yorston, F. H., *Forest Products Lab. Can., Quart. Rev.*, No. 7, 12 (1931).
51. Rutherford, H. A., and Harris, M., in E. Ott: *Cellulose and Cellulose Derivatives*, New York, 1943, p. 180.
52. Jackson, E. L., and Hudson, C. S., *J. Am. Chem. Soc.* **58**, 378 (1936); **59**, 994, 2049 (1937); **60**, 989 (1938).
53. Heidt, L. J., Gladding, E. K., and Purves, C. B., *Tech. Assoc. Papers* **28**, 178 (1945).
54. Pacsu, E., *Textile Research J.* **15**, 354 (1945).
55. Bergek, T., Gustavsson, S., and Lindvall, E., *Svensk Papperstidn.* **50**, No. 11B, Jubilee Vol. E. Hägglund, 22 (1947).
56. Davidson, G. F., *J. Textile Inst.* **25**, T174 (1934); **29**, T195 (1938); **31**, T181 (1940).
57. Opfermann, E., and Hochberger, E., *Die Bleiche des Zellstoffs*, Berlin, 1935-1936, part II, p. 113.
58. Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.* **18**, T135 (1927).
59. Casciani, F., and Storin, G. K., *Paper Trade J.* **115**, No. 14, 89 (1942).
60. Opfermann, E., and Hochberger, E., *Die Bleiche des Zellstoffs*, Berlin, 1935-1936, part I, p. 237; German Pat. 436,804 (1927).
61. Toovey, T. W., *Paper Trade J.* **114**, No. 7, 23 (1942).
62. Chilson, W. A., *Paper Trade J.* **109**, No. 25, 29 (1939).
63. McCarthy, J. L., Hibbert, H., and Tomlinson, G. H., U. S. Pat. 2,226,356.
64. Rue, J. D., and Nagel, S. C., *Paper Trade J.* **114**, No. 24, 26 (1942).
65. Wells, D. S., and Schelhorn, F. B., *Paper Trade J.* **115**, No. 7, 35 (1942).
66. Moffitt, J. E., *Pacific Pulp & Paper Ind.* **13**, No. 6, 23 (1939).
67. Oleskevich, V., *Pulp & Paper Mag. Can.* **48**, No. 3, 123 (1947).
68. Schmidt, E., *Ber.* **54**, 1860 (1921).
69. Hamburger, R., and Kaesz, S., German Pat. 413,338 (1925).
70. Holst, G., *Svensk Papperstidn.* **50**, 472 (1947).
71. Sevón, J., *Kemian Keskusliiton Julkaisuja (Finland)* **10**, No. 7 (1945).
72. Woodward, E. R., *Chem. Eng. News* **22**, 1092 (1944).
73. Vincent, G. P., *Chem. Inds.* **47**, 280 (1940).
74. Giertz, H. W., *Meddelande fran Cellulosaindustriens Centrallaboratorium*, Ser. B, No. 10 (1946).
75. Mathieson Alkali Works, Swedish Pat. 101,127 (1941).
76. Holst, G., *Svensk Papperstidn.* **48**, 23 (1945).

77. White, J. F., Taylor, M. C., and Vincent, G. P., *Ind. Eng. Chem.* **34**, 782 (1942).
78. Taylor, M. C., White, J. F., and Vincent, G. P., *Tech. Assoc. Papers* **23**, 251 (1940).
79. Brennan, J. E., MacMahon, J. D., and Vincent, G. P., *Paper Trade J.* **115**, No. 21, 25 (1942).
80. Taylor, M. C., White, J. F., Vincent, G. P., and Cunningham, G. L., *Ind. Eng. Chem.* **32**, 898 (1940).
81. Vincent, G. P., Russel, L. E., and Woodside, V., *Paper Trade J.* **121**, No. 20, 25 (1945).
82. Vincent, G. P., *Paper Trade J.* **124**, No. 26, 53 (1947).
83. Schmidt, E., *Ber.* **56**, 25 (1923).
84. Jeanes, A., and Isbell, H. C., *J. Research Natl. Bur. Standards* **27**, 125 (1941).
85. White, J. F., and Vincent, G. P., *Tech. Assoc. Papers* **24**, 571 (1941).
86. Lawrence, W. P., *Paper Trade J.* **124**, No. 21, 38 (1947).
87. Opfermann, E., and Hochberger, E., *Die Bleiche des Zellstoffs*, Berlin, 1935/1936, part II, p. 84.
88. Mark, H., in E. Ott: *Cellulose and Cellulose Derivatives*, New York, 1943, p. 1008.
89. Kress, O., and Voigtman, E. H., *Paper Trade J.* **97**, No. 7, 29 (1933).
90. Burgstaller, F., and Sonderhoff, R., *Zellstoff u. Papier* **21**, 46 (1941).
91. Frankevics, J., and Bearse, N. J., *Paper Trade J.* **113**, No. 8, 27 (1941).
92. Samuelson, O., *Svensk Kem. Tid.* **59**, 105 (1947).
93. Opfermann, E., and Hochberger, E., *Die Bleiche des Zellstoffs*, Berlin, 1935/1936, part II, p. 138.
94. Giertz, H. W., *Svensk Papperstidn.* **48**, 317 (1945).
95. Wenzl, H., *Papier-Fabr.* **39**, 177 (1941).
96. Hägglund, E., U. S. Pat. 1,792,009 (1931).

CHAPTER IX

THE CHEMICAL PROCESS IN THE CARBONIZATION OF WOOD

The dry distillation of wood, mainly for the purpose of obtaining charcoal, is a very old art. Wood charcoal was used for metallurgical purposes in earliest antiquity. But not only the charcoal, but also the tar formed during the distillation was prized as an impregnating material for wood.

The carbonization was originally carried out in circular stacks, the oven process being introduced only gradually¹ as the desirability was recognized of obtaining a larger yield of tar, and of recovering the other volatile products formed. The rapidly growing chemical industry, in particular, offered an evergrowing market for these latter products, wood spirits, acetone, and acetic acid. The technique of distillation in a closed space and the recovery of the by-products have been perfected in every respect during the last half-century (1). There has been an urgent economic necessity for this, if the competition of synthetic methanol, acetone, and acetic acid was to be met. An additional factor was the concurrent shrinkage in the market for wood charcoal, at least in some countries, brought about by changes in the steel industry. This point will not be discussed in detail here.

We shall deal here only with the questions of the chemical course of the carbonization, and with the yields and properties of the products formed.

The processes involved in the thermal decomposition of wood are extremely complicated, and can scarcely be explained in full. Even at a temperature of a little over 100° C., a loss in the weight of the wood becomes detectable, and the higher the temperature is raised, the more noticeable does this loss become. However, this low-temperature weight-loss does not greatly affect the composition of the wood. But at a temperature of about 275° C., a violent reaction begins (2). P. Klason, G. v. Heidenstam, and E. Norlin (3) have made precise studies of the temperature dependence of the reaction rate, and found that the speed of decomposition increases greatly at 250° C (4). At 300° C the velocity of the reaction has reached

¹ For the history of the development of the wood distillation industry, see Klar, M. *Technologie der Holzverkohlung*, Berlin, 1921; Bunbury, H. M., *The Destructive Distillation of Wood*, London, 1923.

a maximum, but the temperature must be raised to at least 350° C to obtain usable charcoal.

The heat produced by the reaction can raise the temperature to approximately 400° C during the carbonization, even if heat is not applied from the outside.

As far as the course of the reaction is concerned, P. Klason (5) has shown that the dry distillation occurs in two stages, called the primary and the secondary stages. The primary reactions alone occur when wood is distilled in a high vacuum; under these conditions the decomposition of the wood proceeds as shown in the following table:

Original Material (Birch Wood)	Products	Yield %
$2C_{42}H_{60}O_{28}$ (= 100%)	$3C_{10}H_5O$ —Primary charcoal	20.8
	$19H_2O$ —Primary water	16.8
	$3CO_2$ —Primary carbon dioxide	6.5
	$2.5CH_3COOH$	7.5
	$HCOOH$	2.2
	CH_3OH	1.6
	$C_{36}H_{43}O_{16}$ —Primary tar (pitch)	36.0
	C_5H_8O —Primary tar oils, formaldehyde, etc.	4.2

In the secondary stage, the tar is further decomposed, in the following way:

Tar 36 %	Products	Yield %
$C_{30}H_{20}O_3$ —	Secondary charcoal	21.1
	Water	8.0
	Carbon dioxide	4.3
	Hydrocarbons	2.8

The formation of acetic acid, formic acid, formaldehyde, wood spirit, i.e., methyl alcohol, and acetone, under various conditions was also studied. The results of the experiments are collected in the following table:

Dry Distillation of Birch Wood

Maximum Temperature 400° C

Yields in % of Weight of Dry Wood (Free of Ash)

Product	Cathode-Ray Vacuum	5 mm. Hg. 5 hrs. Heating	Atm. Press. 3 hrs. Heating	Atm. Press. 8 hrs. Heating	Atm. Press. 16 hrs. Heating	Atm. Press. 14 days Heating
Charcoal.....	19.38	19.54	25.51	30.85	33.18	39.44
Tar.....	43.66	37.18	18.0	16.94	10.1	1.8
Acids (determined as acetic acid by titra- tion).....	10.20	10.05	7.42	7.57	7.30	6.91
Acetic acid.....	7.05	7.05	6.50	6.77	6.58	6.48
Formic acid.....	2.40	2.30	0.71	0.61	0.55	0.33
Wood spirit.....	—	1.23	1.65	1.67	1.72	1.76
Methyl alcohol.....	—	1.20	1.49	1.47	1.50	1.41
Acetone.....	—	0.03	0.16	0.20	0.22	0.35
Formaldehyde.....	1.27	1.20	1.00	0.90	—	0.80

According to these experiments, the quantities of acetic acid and of methyl alcohol formed would be almost independent of the speed of carbonization (the time taken to raise the temperature uniformly from 250°C to 400°C). This is not in agreement with the results of other investigators like M. Senff (6), E. Barilot (7), E. Norlin (8), and E. Borghensam (9).

The yield of formic acid, furthermore, is greatest in the vacuum distillation, according to Klason's figures, and decreases when the speed of carbonization is decreased.

The acetone produced by vacuum distillation was negligible, but under atmospheric pressure the yield rose from 0.15% to 0.3%, as the rate of carbonization was decreased. From these results it was concluded that the acetone is a secondary product, formed from acetic acid.

According to Klason, when the dry distillation proceeds slowly, all the reactions which occur at the temperature of the distillation run to completion, and the reaction products are therefore stable. This is reflected particularly in the yield of charcoal, which then reaches its maximum of 40%, while the tar finally disappears completely. The slow distillations also give the greatest quantities of water (26%), and of carbon dioxide (approx. 12%).

Under the conditions prevailing during the carbonization of wood, the first stage of the reaction—formation of the primary charcoal and of primary tar—is immediately accompanied by the second stage, so that as soon as the primary tar is formed, it decomposes into secondary tar, charcoal, and gas. This can be seen from the fact that the outsides and the insides of the lumps of ordinary charcoal do not differ in appearance. The charcoal formed from tar during the second stage of the reaction must, therefore, be deposited evenly throughout the charcoal (10).

The yield of charcoal is extremely dependent on the final temperature attained. This is made clear by the following figures of P. Klason and Å. Bergh (11):

Carbonization Temperature °C.	Carbonization Time in hrs.	Yield in %	Composition of the Charcoal	
			% C	% H
200	48	91.8	52.3	6.3
250	48	65.2	70.6	5.2
300	24	51.4	73.2	4.9
400	5	40.6	77.7	4.5
500	—	31.0	89.2	3.1
600	—	29.1	92.2	2.6
700	—	27.8	92.8	2.4
800	—	26.7	95.7	1.0
900	—	26.6	96.1	0.7
1,000	—	26.8	96.6	0.5
1,100	—	26.1	96.4	0.4

According to these figures, the charcoal formed at 400°C is not stable at higher temperatures.

The composition of the tar, too, is very much dependent on the temperature. Some of the substances present in the tar are unstable, and are easily resinified. If the tar is "cracked" by heating under pressure, hydrocarbons and phenols are the principal products.

Not only the conditions of carbonization, but also the kind of wood used, has a bearing on the composition of the tar (12) as may be seen from the following table:

Type of Wood	Unsapon- ifiable %	Anhydrides of Hydroxy Acids %	Hydroxy Ether- Insol. %	Acids Ether- Sol. %	Resin Acids %	Fatty Acids %	Phenols %
Beech.....	18	9.5	33.3	19	7.7	3.2	9.3
Resinous pine	53.5	0	44		17	6	9.5

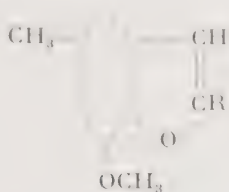
It is interesting to know from which of the constituents of wood the various products mentioned above arise, and by what processes. The water is, of course, split off in dehydration reactions, and the methyl alcohol arises from the methoxyl groups of the wood (pure cellulose yields no methyl alcohol). Acetic acid may be formed partly from the lignin and partly from the carbohydrates. O. Aschan (13) formulates the production of acetic acid and its homologues as follows:



It has been established that hardwoods and the cellulose derived from hardwoods, both of which have a very high pentosan content, give appreciably more acetic acid than softwoods and softwood cellulose [Klason (3)]. It is therefore natural to assume that most of the acetic acid is derived from the pentosans and from the lignin of the wood (14).

The tar is derived from all the chief organic constituents of the wood—carbohydrates, lignin, and resin. The carbohydrates yield, for the most part, only aliphatic compounds (15), but the lignin gives rise to large quantities of aromatic substances. The latter consist mainly of phenols, both simple and complex. P. Klason (16) has pointed out that many of these phenols are substituted in the 1, 3, and 4 positions (e.g., protocatechuic acid).

A. v. Wacek and E. Nittner (17) proved indirectly the presence of various coumarones, but especially of a methoxylated coumarone in the tar from beech wood. After ozonization of the neutral fraction they isolated 2-hydroxy-3-methoxy-5-methylbenzoic acid, which can arise from a substituted coumarone of the following constitution:



v. Wacek considered this to be evidence in support of Freudenberg's theory (18), which postulates that in the lignin molecules besides the ether linkages between the units there also occurs C - C condensation in a position ortho to the ether bridges. However, as v. Wacek emphasizes, it seems also possible that the furan ring arises during the dry distillation.

Furfural and various other furans should also be mentioned among the numerous decomposition products of wood. It is reasonable to assume that a great part of these substances is derived from the pentosan. The higher ketones are probably formed, like acetone, from the corresponding carboxylic acids.

The water phase of wood distillates ("pyroligneous acid") yields on redistillation a tarry residue called "dissolved tar". Its composition has recently been investigated by N. Hellström (19). Among other substances he proved the presence of levulinic and glycolic acids, valerolactone, methyleyclopentenolone, maltol and levoglucosan. On heating and digestion with strong acids, about 50% of the tar could be converted into humic substances. This humification may be related to the reactions leading to the "tar elimination" described by D. F. Othmer and R. Katzen (20), which consists in heating the pyroligneous acid after addition of sulfuric acid.

Carbon dioxide, carbon monoxide, methane and other hydrocarbons, and hydrogen are the principal gases formed during the carbonization of wood.

H. Bergström (21) gives the following figures for the composition of the non-condensable gas produced from spruce and pine in various distilling ovens:

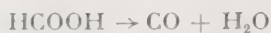
	Volume per cent
Carbon dioxide.....	50-56
Carbon monoxide.....	28-30
Methane.....	11.5-18
Other hydrocarbons.....	2-3
Hydrogen.....	0.5-1

The total weight of gases was 16-18% of the weight of the wood.

P. Klason (16) is of the opinion that the carbon dioxide is produced by decarboxylation of non-volatile carboxylic acids, according to the equation



He thinks that carbon monoxide might arise at least partly from formic acid, by the reaction



According to L. F. Hawley and S. S. Ayar (22) the methane probably comes chiefly from the methoxyl groups of the wood. Not less than two-thirds of the methoxyl groups of the wood are necessary to produce the methane observed. Only a small fraction of the methoxyl groups are converted into methyl alcohol.

P. Klason, G. v. Heidenstam, and E. Norlin (3) obtained the following yields on distilling various kinds of woods:

Product	Type of Wood			
	Pine %	Spruce %	Birch %	Beech %
Charcoal.....	37.83	37.81	31.80	34.97
Gases:				
Carbon dioxide.....	10.13	10.30	9.96	10.90
Ethylene.....	0.23	0.20	0.19	0.20
Carbon monoxide.....	3.74	3.78	3.32	4.22
Methane.....	0.59	0.62	0.54	0.47
Methyl alcohol.....	0.88	0.96	1.60	2.07
Acetone.....	0.18	0.20	0.19	0.20
Methyl acetate.....	0.01	0.02	0.02	0.03
Acetic acid.....	3.50	3.19	7.08	6.04
Organic substance contained in sodium salts of water-soluble acids.....	8.03	7.75	8.15	5.89
Tar.....	11.79	8.08	7.93	8.11
Water.....	22.27	25.70	27.81	26.58
Losses.....	0.82	1.39	1.41	0.32

L. F. Hawley and R. C. Palmer (23) have carried out dry distillation of a large variety of American hardwoods, investigating heartwood as well as sapwood. It turned out that sometimes the heartwood, and sometimes the sapwood gave the higher yields of methanol, acetic acid, tar, and charcoal, and no regularity could be observed.

Average Yields from Heartwood and Sapwood

Type of Wood	Wood Spirit %	Acetic Acid %	Charcoal %	Tar %
Beech.....	1.87-2.16	5.87-5.99	41.2-41.4	10.0-10.1
Birch.....	1.54-1.60	6.15-6.80	37.0-38.5	9.0-11.4
Maple.....	1.86-1.93	5.24-5.55	38.9-42.3	10.8-12.4
Red gum.....	1.75	5.46	42.2	9.6
Chestnut.....	0.89	5.36	50.4	3.7-4.7
White oak.....	1.33-1.39	4.29-4.87	44.1-50.0	5.4-9.0
Tupelo.....	1.71	4.84	46.0	11.7
White elm.....	1.90	6.50	39.8	11.6
Slippery elm.....	1.91	5.65	42.4	8.3
Silver maple....	1.83	5.81	42.9	10.1
Green, blue, and yellow ash....	1.67	4.39	43.4	9.6
Black ash.....	1.91	5.40	39.3	10.2
Chestnut oak....	1.27	4.90	43.2	9.5
Swamp oak.....	1.40	5.16	46.9	8.1
Eucalyptus.....	1.50	4.94	46.2	6.3

R. W. Merritt and A. A. White (24) treated oak wood with superheated steam at various temperatures. Decomposition began below 180° C. Most of the pentosan decomposed at 240° C; the condensate at this temperature contained about three-fourths of the total acids and approximately half of the furfural, but no methyl alcohol. Exothermic reactions began in the region 240-260° C., and the cellulose decomposed completely, but only a third of the total methyl alcohol appeared. The main fraction of the methyl alcohol came over only above 280° C.

Repeated attempts have been made to increase the yields of various by-products by adding certain materials, such as sulfuric or phosphoric acids, to the wood. E. C. Palmer (25) tested these acids, and found that they did not increase the yield of acetic acid; on the contrary, sulfuric acid decreased the yield. Phosphoric acid improved the yield of methyl alcohol when the distillation was carried out under pressure. The process has no commercial interest, especially since sulfur and phosphorus constitute undesirable impurities in charcoal which is to be used in metallurgy. L. F. Hawley (26) has tested a large number of substances for "catalytic effect," and found that small quantities of soda or sodium silicate were helpful. His results are given below.

Type of Wood	Addition	Methyl Alcohol	Acetic Acid
Maple.....	—	1.61	5.22
".....	0.5 % Na_2CO_3	1.61	5.32
".....	1.0 % Na_2CO_3	1.94	5.02
".....	1.5 % Na_2CO_3	2.39	5.26
".....	3 % Na_2SiO_3	2.21	5.77
White Oak.....	—	1.17	4.91
" ".....	0.5 % Na_2CO_3	2.58	5.09

The increases in the yield were in all cases so small that this procedure can scarcely be said to have any practical value. Experiments on distillation with superheated steam (27) have not given results of technical value either.

The thermochemistry of wood carbonization has been largely worked out by P. Klason and his co-workers. They determined the heat of reaction by carrying out the carbonization under various conditions, and studying the complete heat balances. To find the heat actually evolved on carbonization one must subtract from the heat of reaction the heat absorbed in heating the reaction products to about 275° C., minus the heat consumed in raising the wood to this temperature. The following results were obtained in the experiment on birch wood mentioned above:

	5 mm. Hg	Atmospheric Pressure 8 hrs. Carbonization	14 days Carbonization
Heat of reaction per kg. of wood, in Calories	+ 123.1	+ 258.6	+ 340.9
in % of the heat of combustion of the wood	+ 2.6	+ 5.3	+ 7.1
Heat evolved, in Calories.....	— 47.6	+ 96.7	+ 169.2
in % of the heat of combustion of the wood	— 1.0	+ 2.0	+ 3.5

It appears from these data that the primary decomposition of the wood does not result in the evolution of heat. The secondary reaction, however, insures a liberation of heat in the over-all process when wood is carbonized at atmospheric pressure. When, in the charcoal pit, the exothermic carbonization reaction proceeds rapidly, an explosion-like phenomenon — “blow off” — occurs. The heat developed by the exothermic reaction has a practical importance in oven coking, since it permits the water in damp wood to be evaporated. At the same time, the moisture of the wood acts as a regulator for the speed of the carbonization (Klason).

Recently, the thermochemistry of wood carbonization has been re-investigated by T. Widell (28) as well as by W. Jensen (29). Their results were in rather good agreement with those obtained by Klason.

Wood charcoal retains the structure of the wood, but this organization is destroyed if the wood is compressed during the carbonization. It appears as if the wood were slightly plastic during one particular stage of the decomposition (30).

The elementary composition of charcoal from various sources is quite similar, as may be seen from the following figures of Klason (3):

Type of Wood	Composition		Calorific Value (cal./g.)
	% C	% H	
Pine.....	82.5	4.0	7,685
Spruce.....	82.5	4.1	7,695
Birch.....	82.2	3.8	7,680
Beech.....	82.1	4.1	7,555

A question which has in a strict sense nothing to do with wood carbonization, but which is worth mentioning in this connection, is that of the changes occurring in wet wood chips when they are stored in large piles. Under these circumstances a great increase in temperature, leading to carbonization sometimes occurs, followed finally by spontaneous combustion. H. Bergström (31) studied this phenomenon in detail.

The first step in the decomposition is initiated by microorganisms. This causes a rise in temperature. At the same time the wood is oxidized directly by the oxygen of the air; this causes a further increase in temperature. As long as the wood contains water, the temperature can not exceed 100° C., but after all the water has been driven out, the temperature rises rapidly, and reaches the point necessary for carbonization. The region of carbonization advances toward the direction from which the air enters (just as it does in the charcoal pits), and when the zone of carbonization comes into contact with the air, ignition occurs. Acetic and formic acids are formed in this process, along with other materials.

REFERENCES

1. Klar, M., and Bunbury, H. M., see footnote to first page of this chapter; Bergström, H., *Handbok för kolare*, fourth ed., Uppsala, 1947; Hawley, L. F., *Wood Distillation*, New York, 1923; Klason, P., *Kolning och torrdestillation av ved etc.*, Stockholm, 1919; Bugge, G., *Industrie der Holzdestillationsprodukte*, Dresden, 1927; cf. also Klar, M., *Holz Roh- u. Werkstoff* **1**, 139 (1938).
2. Chorley, J. C., and Ramsay, W., *J. Soc. Chem. Ind. London* **11**, 395 (1892).
3. Klason, P., Heidenstam, G. v., and Norlin, E., *Arkiv Kemi, Mineral. Geol.* **3**, No. 1 (1907); **3**, No. 10 (1908).
4. Cf. also Violette, H., *Compt. rend.* **32**, 714 (1851).
5. Klason, P., *Arkiv Kemi, Mineral. Geol.* **5**, No. 7 (1913).
6. Senff, M., *Ber.* **18**, 60 (1885).
7. Barilot, E., *Compt. rend.* **122**, 467, 735 (1896.)
8. Norlin, E., *Jernkontorets Ann.* **9**, 783 (1908).
9. Borghensam, E., *Chem. Ztg.* **34**, 609 (1910).
10. Hawley, L. F., in Wise, L. E., *Wood Chemistry*, New York, 1946, p. 682.
11. Klason, P., and Bergh, A., *Arkiv Kemi, Mineral. Geol.* **3**, No. 23 (1909).
12. Cf. Marcusson, J., and Picard, M., *Z. angew. Chem.* **34**, 201 (1921).
13. Aschan, O., *Z. angew. Chem.* **26**, 711 (1913).
14. Cf. also Heuser, E., and Scherer, A., *Brennstoff-Chem.* **4**, 97 (1923); Hawley, L. F., and Aiyar, S. S., *Ind. Eng. Chem.* **14**, 1056 (1922).
15. Erdmann, E., and Schaefer, C., *Ber.* **43**, 2398 (1910); Wichelhaus, H., *Ber.* **43**, 2922 (1910).
16. Klason, P., *Beiträge zur Kenntnis der chemischen Zusammensetzung des Fichtenholzes*, Berlin, 1911.
17. Wacek, A. v., and Nittner, E., *Cellulosechemie* **18**, 29 (1940); cf. also Frankl, H., *Dissertation*, Munich, 1914.
18. Freudenberg, K., Meister, M., and Flickinger, E., *Ber.* **70**, 500 (1937).
19. Hellström, N., *Transactions Roy. Inst. Technol.*, Stockholm, No. 4 (1947).
20. Othmer, D. F., and Katzen, R., *Ind. Eng. Chem.* **35**, 288 (1943).
21. Bergström, H., and Wesslén, G., *Om träkolning*, 3rd. ed. Stockholm, 1923, p. 243.
22. Hawley, L. F., and Aiyar, S. S., *Ind. Eng. Chem.* **14**, 1056 (1922).
23. Hawley, L. F., *Wood Distillation*, New York, 1923, p. 44.
24. Merritt, R. W., and White, A. A., *Ind. Eng. Chem.* **35**, 297 (1943).
25. Palmer, E. C., *Ind. Eng. Chem.* **10**, 264 (1918).
26. Hawley, L. F., *Ind. Eng. Chem.* **14**, 43 (1922).
27. Cf. Büttner, G., and Wislicenus, H., *J. prakt. Chem.* **79**, 177 (1909).
28. Widell, T., *Ing. Vetenskaps Akad. Handl.* No. 199 (1948).
29. Jensen, W., *Acta Acad. Aboensis, Math. Phys.* **16**, No. 3, 48, 121 (1948); *Paper and Timber* (Finland) **32**, 3 (1950).
30. Hawley, L. F., *Ind. Eng. Chem.* **13**, 301 (1921).
31. Bergström, H., *Third International Conference on Bituminous Coal*, Pittsburgh, 1931.

CHAPTER X

UTILIZATION OF WOOD BY CAUSTIC FUSION.
PRESSURE HEATING WITH ALKALI. AND DIGESTION
WITH TARS OR PHENOLS

I. Caustic Fusion

Oxalic acid was once produced exclusively by the caustic fusion of wood. The reaction involved has been studied by many workers, chiefly with a view to determining the best conditions for obtaining the highest possible yield. L. Possoz (1) found that 100 parts of sawdust, when heated with 300 parts of potassium hydroxide for 4 hours at 200-225° C., yielded 70 parts of crystalline oxalic acid. Using mixtures of sodium and potassium hydroxides, he found that the best yield of oxalic acid was obtained when the ratio KOH : NaOH was 2 : 1. His finding that the use of sodium hydroxide alone was not advantageous, was confirmed by W. Thorn (2). Thorn stated that the yield of oxalic acid increased continuously when the ratio KOH : NaOH was increased, until the potassium hydroxide reached 40% of the total alkali. The oxalic acid obtained at a working temperature of 240-250° C. was then 80% of the air-dry weight of the wood. Further addition of potassium hydroxide had no favorable influence. He also investigated the behavior of various kinds of wood, and found that beech and oak gave 10% higher yields than spruce, pine, and poplar. In these experiments the alkali (100 g. per 50 g. of air dried sawdust) was added in the form of an aqueous solution (d. 42° Baumé). The time of the reaction was 1½ hours. The use of hot air or the addition of manganese dioxide (MnO₂) did not increase the yield of oxalic acid.

The production of oxalic acid was investigated later by A. v. Hedenström (3). He first studied the formation of oxalic acid from pure cellulose (cotton wool), and found that the yield was not improved by increasing

the quantity of caustic alkali used beyond four times the weight of the cellulose. The best yield was obtained when the temperature was raised gradually to 280°C. with constant stirring. Under these conditions 3.72 g. of crystalline oxalic acid was obtained from 3 g. of cotton, but at a temperature of 225°C. only 1 g. was obtained. Hedenström believes that intermediates are formed at a temperature of about 200°C. which are converted to oxalic acid at a temperature of about 250°C. This seems also to be true for wood fused with alkali. Hedenström found, for example, that when oak chips were fused with four parts of potassium hydroxide, the yield of oxalic acid at 235-240°C. was only 77% of the weight of the wood, but that at 280°C. it was 122%. He also reported that the addition of oxidizing agents, such as potassium permanganate or lead peroxide, increased the yield by 10-15%.

W. Qvist (4) found that the yield of oxalic acid on fusion with KOH at 190-200°C. amounts to 80-100% when 2-2.5 parts of potassium hydroxide is taken to one part of sawdust. If less potassium hydroxide is used, charring is difficult to avoid. When large quantities of potassium hydroxide are used, the yield drops, unless the temperature is increased. Mixtures of potassium and sodium hydroxides give maximum yields when there are seven equivalents of potassium hydroxide to three equivalents of sodium hydroxide. Birch, oak, aspen, spruce, and pine give the same yields; approximately the same amount of oxalic acid is also produced from hydrocellulose.

When the fusion is carried out with sodium hydroxide alone, it is necessary to use 2.35-2.80 parts of alkali to one part of sawdust; otherwise it is impossible to avoid charring. The interesting observation was made that the addition of inert materials, e.g. salt or sand, caused the yield of oxalic acid to increase.

E. Heuser and F. Herrmann (6) have studied the individual constituents of wood with respect to their convertibility into oxalic acid. As far as the lignin is concerned, E. Heuser and A. Winsvold (7) have confirmed earlier reports that lignin gives no oxalic acid when air is excluded, but that in the presence of air oxalic acid is formed in about 20% yield. Cellulose gave a 90% yield, and wood flour from spruce at most 65%. A. v. Hedenström (3) had previously observed that the yield of oxalic acid is increased by the admission of air.

Other investigations were carried out by S. A. Mahood and D. E. Cable (5). They submitted various kinds of wood to caustic fusion using 3 parts of NaOH to 1 part of wood and obtained, besides oxalic acid, other decomposition products, particularly acetic acid, in the yields shown in the following table:

Type of Wood	Time of Heating hrs.	170° C		200° C		230° C	
		Acetic Acid %	Oxalic Acid %	Acetic Acid %	Oxalic Acid %	Acetic Acid %	Oxalic Acid %
White oak...	$\frac{3}{4}$	4.1	6.6	5.9	12.5	11.0	37.5
	$1\frac{1}{2}$	4.3	6.6	7.1	19.6	12.0	39.5
	3	6.4	24.1	10.2	31.5	17.0	38.4
	6	8.4	—	13.6	55.3	17.6	33.3
	12	11.4	38.0	15.6	62.5	18.9	40.4
Hard maple .	$\frac{3}{4}$	4.3	—	7.3	—	11.5	—
	$1\frac{1}{2}$	4.7	—	10.0	24.9	14.1	42.0
	3	5.3	—	12.8	46.4	17.8	58.7
	6	8.1	—	15.7	59.3	18.1	46.4
	12	7.2	—	16.3	—	19.1	—
Elm.....	$\frac{3}{4}$	6.7	—	9.9	—	12.8	—
	$1\frac{1}{2}$	6.1	—	9.9	26.8	15.5	33.9
	3	7.8	—	11.2	34.6	19.1	56.1
	6	8.6	—	14.4	73.6	18.7	50.6
	12	9.5	—	13.9	—	18.5	—
Longleaf pine	$\frac{3}{4}$	2.2	1.5	4.2	14.9	7.9	43.6
	$1\frac{1}{2}$	2.3	2.2	4.1	13.5	9.4	54.6
	3	3.1	6.5	6.4	30.0	12.0	68.9
	6	8.4	37.2	14.4	70.0	14.0	69.3
	12	12.6	58.0	14.7	74.0	14.6	67.4

It should be emphasized that these experiments were undertaken in an effort to obtain acetic acid from wood wastes; oxalic acid was therefore considered to be only a by-product. Methyl alcohol was also obtained in a yield equal to about 2.4% of the weight of the wood.

The formation of acetic acid on caustic fusion of carbohydrates had been investigated earlier by C. F. Cross, E. J. Bevan, and J. F. V. Isaac (8). They obtained a yield of 18-28% from pine, which seems very large by comparison with the results of Mahood and Cable. They also established the fact that the yield of acetic acid was dependent on the ratio between the amounts of alkali and of wood.

Although considerable quantities of acetic acid were obtained in the experiments of Mahood and Cable, it was quite clear that this procedure had no economic prospects unless the alkali could be recovered. The authors believed that they had solved this problem, but so far as is known, the procedure has not yet had any practical success.

D. F. Othmer, C. H. Gamer, and J. J. Jacobs (9), D. F. Othmer, J. J. Jacobs, and A. C. Pabst (10), and D. F. Othmer and R. H. Royer (11) have investigated the caustic fusion of sawdust and obtained under optimum conditions—heating three hours at 200°C a mixture of three parts of sodium hydroxide to one part of dry sawdust—45.5% oxalic acid, 11.7% acetic acid, 2.5% formic acid, and 5.5% methyl alcohol. The possibility of making the process continuous was tested in a pilot plant.

After the fusion the mass was extracted with water, and the solution concentrated until the bulk of the sodium salts of oxalic, acetic, and

formic acids separated out. They were centrifuged off, and the solution, containing unchanged sodium hydroxide and some sodium acetate, was further concentrated and used again for the decomposition of wood.

It was not shown, however, whether this method could compete with the usual synthetic process for oxalic acid, in which carbon monoxide is added to sodium hydroxide under elevated pressure and temperature and the formate obtained is converted at 400°C into oxalate and hydrogen.

Of other methods proposed for producing oxalic acid, the oxidation of carbohydrate materials like starch, cellulose, and wood wastes with nitric acid in the presence of vanadium oxides as catalysts should be mentioned. The difficulties encountered in the recovery of the nitrogen oxides seem to have limited the commercial use of this process.

II. Alkaline Pressure Heating

F. Fischer, H. Schrader, and W. Treibs (12) found that both cellulose and lignin yielded considerable quantities of acetic acid on oxidation under pressure. Heating under pressure in alkaline solution without oxidation also gave rise to acetic acid, though in appreciably smaller quantities. E. Hägglund investigated this problem systematically (13). His results are given in part in the following table:

Spruce

Pulping for 8 hrs. at 200°C with Sodium Hydroxide Corresponding to 48% of the Dry Weight of the Wood; Ratio Wood : NaOH Solution 1 : 6; 19.1% Undissolved. Black Liquor Heated Under Pressure to 350°C.

Further Addition of Alkali Before Pressure Heating g./100 g. Wood	Time of Pressure Heating min.	Gas l. 100 g. Wood	Tar and Pitch g. 100 g. Wood	Acetic Acid g. 100 g. Wood	Formic Acid g. 100 g. Wood	Methyl Alcohol g. 100 g. Wood	Acetone g. 100 g. Wood	Degree ¹ of Decarbonization
No Pressure Heating.....	—	—	—	4.77	3.6	0.97	0.12	—
0.....	0	5.9	26.8	6.54	0.94	1.38	0.58	84.5
10.....	0	6.5	22.1	7.10	2.09	1.35	0.54	77.5
30.....	0	11.6	10.3	11.50	3.24	1.63	0.41	61.8
0.....	15	13.0	26.2	12.62	0.61	1.52	0.77	—
10.....	15	8.4	25.6	15.36	1.34	1.25	0.74	90.5
30.....	15	8.9	23.8	11.78	1.96	1.29	0.76	90.5

Birch

Pulping for 8 hrs. at 200°C with Sodium Hydroxide Corresponding to 50% of the Dry Weight of the Wood; Ratio Wood : NaOH Solution 1 : 6; 7.9% Undissolved. Black Liquor Heated Under Pressure to 350°C.

No Pressure Heating.....	—	—	—	9.83	5.82	0.37	0.04	—
0.....	0	8.48	27.8	10.17	3.25	1.43	0.46	87.4
10.....	0	7.62	—	11.17	2.29	1.42	0.32	85.2
20.....	0	8.42	—	11.85	2.81	1.26	0.42	—
0.....	15	10.58	23.0	11.93	3.69	1.03	0.30	93.2
10.....	15	9.54	24.8	12.92	2.86	1.15	0.52	90.0

Beech

Pulping for 8 hrs. at 190° C with Sodium Hydroxide Corresponding to 46% of the Dry Weight of the Wood; Ratio Wood : NaOH Solution 1 : 6; 6% Undissolved. Black Liquor Heated Under Pressure to 350° C.

Further Addition of Alkali Before Pressure Heating g./100 g. Wood	Time of Pressure Heating min.	Gas l./100 g. Wood	Tar and Pitch g./100 g. Wood	Acetic Acid g./100 g. Wood	Formic Acid g./100 g. Wood	Methyl Alcohol g./100 g. Wood	Acetone g./100 g. Wood	Degree ¹ of Decarbonization
No Pressure Heating.....	—	—	—	6.91	4.86	0.58	0.03	—
0.....	0	8.44	—	13.10	2.23	1.47	0.92	—
10.....	0	13.60	—	13.20	2.18	1.15	0.53	—
20.....	0	15.78	—	12.38	2.05	0.98	0.64	74.67
0.....	15	13.73	—	21.73	1.21	1.58	1.52	—
10.....	15	16.77	—	21.02	1.75	0.96	1.09	—
20.....	15	19.00	—	20.89	1.63	0.92	0.88	93.18

¹ "Degree of decarbonization" means the difference between the amount (A) of carbon contained in the non-volatile fraction of the original black liquor and the amount (B) of carbon contained in the non-volatile fraction of the pressure-heated solution in per cent of A.

It should be noted that where the "time of pressure heating" is given as "0" this means that the liquor was cooled immediately after the temperature of 350° C had been reached. The gas consisted mostly of hydrogen.

H. Wallin and S. Odén (14) have also carried out experiments along the same lines. The following example may be quoted: 1 part of pine sawdust plus 0.9 parts of sodium hydroxide in 3.9 parts of water was heated 5 hours at 180° C; all was dissolved. Methyl alcohol and acetone were determined in the waste liquor. The liquor was then heated 2 hours under pressure (300-500 atm.). After distilling off the methyl alcohol and acetone formed, the liquor was evaporated down and the residue subjected to dry distillation. The results are given in the following table:

Yields in Per Cent of the Weight of the Wood

Digestion at 180° C		Heating Under Pressure			
Methyl Alcohol	Acetone	Methyl Alcohol	Acetone	Other Products Boiling Below 80° C	Oils
0.73	0.02	1.6	0.11	0.16	0.34

Dry Distillation with Addition of 30% Lime (Based on Wood) Maximum Temp. 500° C

Methyl Alcohol	Acetone	Butanone	Acetone Oils	Light Oils	Heavy Oils
0.85	2.51	2.47	1.40	2.49	13.41

In another experiment, in which a large excess of soda was added before the heating under pressure, the following total yields were obtained:

Product	% of Weight of Wood
Methyl Alcohol.....	1.24
Acetone.....	5.55
Butanone.....	2.80
Light Oils.....	11.00
Heavy Oils.....	14.45
Carbon.....	9.76

Black liquor from the production of soda pulp was treated in the same way. The following yields were reported, in per cent of absolutely dry pulp: methyl alcohol, 3.2; acetone and methyl ethyl ketone, 16.1; steam-distillable oils, 16.9; and other oils, 7.4.

S. Odén treated sawdust with alkali, dissolving it completely. The liquor was evaporated down, and dry-distilled. The following yields were obtained: methyl alcohol, 3.08%, acetone and methyl ethyl ketone, 1.47%, oils and extracts, 3.26% (total 7.81%).

He obtained the following results when the wood was completely dissolved, as described above, then heated under pressure (360-380 C), and finally dry-distilled:

Process	Methyl Alcohol %	Acetone %	Oils, etc. %	Gas %
Pulping.....	1.20	0.05	0.01	0.03
Pressure Heating.....	0.29	0.66	5.17	0.91
Dry Distillation.....	0.36	6.65	18.00	—
Total	1.85	7.36	23.18	0.94

When the cellulose was removed first (yield 46.95%) and the black liquor then heated under pressure and dry-distilled, the yields were:

Process	Methyl Alcohol %	Acetone %	Oils, etc. %	Gas %
Pulping.....	0.10	0.03	—	—
Heating under Pressure.....	0.27	0.44	2.71	—
Dry Distillation.....	0.05	1.96	6.92	19.25
Total	0.42	2.43	9.63	19.25

Pure cellulose and "Willstätter lignin" gave the following yields under the same conditions:

	Methyl Alcohol %	Acetone %	Oils, etc. %	Gas %
Cellulose.....	1.54	3.89	15.61	15.61
Lignin.....	0.70	3.45	12.11	20.52

Odén also attempted to decompose the wood with sodium silicate solution. He succeeded, by working at 150°C with 500 g. of sodium silicate and 1,500 cc. of water per 200 g. of wood. The black liquor was heated under

pressure as before, and the residue dry-distilled. The yields were as follows, in percentages of the weight of the wood:

Process	Methyl Alcohol %	Acetone %	Oils, etc. %	Gas %
Pulping.....	0.32	0.04	—	—
Heating under pressure.....	1.05	0.27	0.66	1.92
Dry distillation.....	0.15	1.09	3.74	30.62
Total	1.52	1.40	4.40	32.54

Odén calls attention to the fact that the yield of products from the individual constituents of the wood, namely cellulose and "non-cellulose" fractions, is appreciably smaller than the yield from the wood directly.

	From Wood %	From Cellulose Plus Non-cellulose %
Acetone.....	7.36	3.91
Methyl alcohol.....	1.85	1.14
Oils.....	22.29	11.72
Total	31.50	16.77

The oils obtained were highly unsaturated, and can, therefore, not be used as motor fuels without further refining. The lighter oils had a specific gravity of about 0.87-0.93. Elementary analysis of the oils gave the following average values: 80% C, 10% H, 10% O.

H. Bergström, K. N. Cederquist and K. G. Trobeck (15) have carried out experiments on the pressure heating of wood (particularly beech) with lime and water. In their experiments 3,010 g. of dry beech wood, 2,643 g. slaked lime, and 444 g. water, heated 2 hours at 250°C and under a pressure of 51 atm., yielded 27 liters of gases, 22.3 g. of oils, and a water solution which on distillation gave 190 g. of organic material. The residue in the autoclave contained 1,818 g. of water-soluble calcium compounds and 3,120 g. of insoluble material.

When the experiment was carried out at 325°C, corresponding to a pressure of 170 atm., for 45 min., there were obtained 125 liters of gases, 224.8 g. of oils, and a water solution from which 406 g. of oils could be distilled. The residue in the autoclave consisted of 980 g. of calcium compounds, and 3,250 g. of insoluble material.

The decomposition was accompanied by an evolution of heat, corresponding to 8-11% of the heat content of the wood.

III. Digestion with Tars and Phenols

When wood is heated to about 280°C with tars or phenols, it is dissolved, forming so-called wood tar-pitch (16). This reaction is accompanied by an

evolution of heat, but only a slight one. The wood tar-pitch is soluble in acetone and other solvents.

When 4.2 kg. of softwood was heated for 3-4 hours at 280-300° C with 6.6 kg. of phenols from tar, 65% of the wood was converted to wood tar-pitch. An additional 14% of gases, consisting chiefly of carbon dioxide, was recovered.

Extremely resinous pine wood could be transformed into a fusible pitch at 300°C, without the addition of solvents.

REFERENCES

1. Possoz, L., *Dinglers Polytech. J.* **150**, 127 (1858); *Compt. rend.* **47**, 207, 648 (1858).
2. Thorn, W., *Dinglers Polytech. J.* **210**, 24 (1873).
3. Hedenström, A. v., *Chem.-Ztg.* **34**, 613 (1910); **35**, 853 (1911).
4. Qvist, W., *Acta Acad. Aboensis, Math. et Phys.* **3**, No. 9 (1924).
5. Mahood, S. A., and Cable, D. E., *Ind. Eng. Chem.* **11**, 651 (1919).
6. Heuser, E., and Hermann, F., *Cellulosechemie* **5**, 1 (1924).
7. Heuser, E., and Winsvold, A., *Cellulosechemie* **4**, 49, 62 (1923).
8. Cross, C. F., Bevan, E. J., and Isaac, J. F. v., *J. Soc. Chem. Ind. London* **11**, 966 (1892).
9. Othmer, D. F., Gamer, C. H., and Jacobs, J. J., jr., *Ind. Eng. Chem.* **34**, 262 (1942).
10. Othmer, D. F., Jacobs, J. J., jr., and Pabst, A. C., *Ind. Eng. Chem.* **34**, 268 (1942).
11. Othmer, D. F., and Royer, R. H., *Ind. Eng. Chem.* **34**, 274 (1942).
12. Fischer, F., Schrader, H., and Treibs, W., *Ges. Abhandl. Kenntnis Kohle* **5**, 220, 311 (1920-21).
13. Hägglund, E., *Svensk Kem. Tid.* **39**, 90 (1927).
14. Wallin, H., and Odén, S., *Ing. Vetenskaps Akad. Handl.* No. 54 (1926).
15. Bergström, H., Cederquist, K. N., and Trobeck, K. G., *Iva* **1936**, 118.
16. Bergström, H., Cederquist, K. N., and Trobeck, K. G., *Iva* **1937**, 84; cf. *Iva* **1930**, 5, and **1931**, 12; cf. also Swedish Pat. 68,423 (1931).

CHAPTER XI

THE BEHAVIOR OF WOOD DURING STORAGE

C. G. Schwalbe (1) has called attention to the changes that occur in wood fibers during storage. He assumes that similar changes also are brought about by the aging of the wood. The "age" of a fiber he defines as the length of time that the fiber has been alive; in this sense the inner rings of the tree are "older" than the outer rings. In his opinion, the aging of wood makes it more difficult to pulp, and the easier pulping of green wood which he observed is due to the fact that "the juices, which contain colloidal materials, have not yet been dried. When the juices are dried, the colloids coagulate, and act as a cement." According to this view, drying the wood would increase the speed of "harmful aging."

As proof of the fact that wood stored in contact with the air is changed, Schwalbe states that wood kept for eight years in the form of chips can no longer be pulped by the sulfite process. Schwalbe found moreover, that wood which had been extracted with benzene or ether could no longer be pulped with acid sulfite. The reason for this is, in his opinion, that the complete dessication of colloidal membranes causes a "hornification" which makes the membranes unable to swell.

E. Hågglund and S. Hansen (2) investigated in detail the behavior of both heartwood and sapwood of spruce during sulfite pulping. The wood was taken from freshly felled trunks, 120 and 52 years old, which had not been floated down streams. Both heartwood and sapwood were pulped under exactly the same conditions, except that stronger acid was used on the 120-year-old trunk. The following results were obtained:

	Wood		
	Moisture Content	Ash	Ether Extractable
120-year-old			
Heartwood.....	12.39	0.41	1.46
Sapwood.....	13.89	0.43	1.49
52-year-old			
Heartwood.....	13.92	0.32	
Sapwood.....	25.01	0.32	

	Pulp Yield in % (Average)	Ash %	Lignin %
120-year-old			
Heartwood.....	48.7	0.97	3.8
Sapwood.....	48.2	0.77	2.8
52-year-old			
Heartwood.....	54.9	1.19	3.9
Sapwood.....	55.7	1.18	3.5

It is evident that no difference between heartwood and sapwood is established, although one would assume from the hypothesis of Schwalbe that the heartwood would be harder to pulp. This would have resulted (since the cooks were terminated at the same time) in a higher yield of pulp from heartwood than from sapwood. Furthermore, the pulp from heartwood would have had a higher lignin and ash content. For all practical purposes, this is obviously not the case.

Schwalbe's theory would also lead one to expect that air-dried wood would be harder to pulp than green wood. Experiments by E. Hägglund (3) do not confirm this. Wood cut from various heights on the trunk was tested both in the green and dried conditions.

Moisture Content of the Wood %			
Center of Trunk Dry	Green	Tip of Trunk Dry	Green
11.8	26.9	6.9	46.5

Yield of Pulp in % of Weight of Dry Wood After Sulfite Pulping

Experiment I			
49.0	49.2	47.3	48.7
Experiment II			
51.2	52.5	49.5	51.8
Experiment III			
49.5	50.4	48.7	49.8

It turned out, then, that the speed of pulping was somewhat greater when the wood was dry; this fact may probably be attributed to the easier diffusion of the pulping liquor into the dry wood.

The changes which occur in wood chips on storage can, therefore, hardly be attributed to a dessication, but probably depend on autoxidations occurring either with the major or the accessory constituents of the wood (4).

It has been known for a long time, and has been shown anew by W. H. Smith (5) that finely divided wood easily undergoes changes, particularly in sunshine. Smith studied the properties of mechanical pulp both before and after the action of sunlight or ozone, or of elevated temperatures.

	Mechanical Pulp in Original Conditional	After 75 hrs. in Sunlight	After Treatment With Air Containing Ozone	After 20 hrs. at 100° C	After 20 hrs. at 150° C
Methoxyl %....	5.10	4.60	4.74	4.75	4.48
Furfural %.....	6.23	5.41	5.82	5.72	4.64
Copper No.....	2.0	7.6	10.9	3.0	11.9
Acid No.....	16.1	51.0	63.2	27.0	63.0

Ordinary cold water is not entirely without effect on wood, as appears from the reports of investigations by A. W. Schorger, by S. A. Mahood and D. E. Cable, and by G. J. Ritter and L. C. Fleck (6). The solubility varies between 1% and 13%. The solubility in hot water is greater. The substances dissolved are chiefly sugars, traces of lignin, methyl alcohol, furfural, and acids like acetic and formic (7). In view of the ease with which acetic acid is formed from wood by hydrolysis it is probable that the action of hot water is to a large extent hydrolytic. Other investigations of the action of hot and cold water on wood are discussed on p. 103.

This question has a practical bearing on the production of "brown mechanical pulp." In this process the wood is usually treated with steam at various temperatures, or, less frequently, heated with water under pressure (Enge process). In the first case, less wood is dissolved. E. Sutermeister (8) reports, for example, that 0.2% of acetic acid and 0.25% of sugar are formed from spruce. These figures are in good accord with those obtained in actual practice. C. Franck (9) obtained on steam treatment from 27 cu.m. of wood:

	kg.		kg.
Volatile acids.....	40.00	Methylfurfural.....	0.15
Sugar.....	80.00	Methyl alcohol.....	5.12
Humus substances.....	147.00	Acetone.....	0.14
Furfural.....	8.80	Amines.....	0.14

H. Bergström (10) found that heating spruce or pine with water for 2 hours under 6 atm. pressure gave 1.2–1.5% acetic acid and 0.2% formic acid, while birch gave 3.13% acetic acid and 0.16% formic acid.

A knowledge of the way in which various woods behave toward solutions of acids and bases is of practical importance. The question is particularly important in chemical industries, where vessels and pipes of wood are frequently used. C. S. Robinson (11) reports that the following woods are most suitable for this purpose:

Louisiana cypress (*Taxodium distichum*), longleaf pine (*Pinus palustris*), California redwood (*Sequoia sempervirens*), white pine (*Pinus strobus*), Douglas fir (*Pseudotsuga taxifolia*), hard maple (*Acer saccharum*),

yellow poplar (*Populus deltoides*), white oak (*Quercus alba*), tamarack (*Larix laricina*), spruce (*Picea rubra*), Norway pine (*Pinus resinosa*).

S. J. Hauser and C. Bahlman (12) have tested six of these woods in the following respects: 1. Extractability of colored substances from the wood 2. Absorption of liquids by the wood 3. Swelling or shrinking of the wood 4. Changes in the strength and hardness of the wood.

The first of these items is of importance when, for example, the wood comes in contact with drinking water, or when it is used in making vessels for washing.

The solubility of the wood in various materials is indicated in the following table by the figures 1 to 4, 1 indicating that the solubility is small, and 4 that it is great.

Solvent	Cypress	Longleaf Pine	Douglas Fir	Red-wood	Hard Maple	White Oak
5% and 25% Acetic acid.....	1	1	1	2	1	2
50% and 100% " "	2	2	2	3	2	3
5% and 25% Hydrochloric acid..	1	1	1	2	1	2
Concentrated hydrochloric acid	1	4	4	4	4	4
10% Sulfuric acid.....	1	1	1	3	1	3
25% " "	2	2	1	3	2	3
5% Nitric acid.....	1	1	4	4	4	4
1% Sodium hydroxide.....	3	3	4	4	4	4
Concentrated sodium hydroxide.....	3	3	4	4	4	4
Saturated lime water.....	2	2	2	3	2	3
5% Bleaching powder solution.....	1	2	2	2	2	2
Sodium sulfide solution.....	1	4	4	4	4	4
5% Soda solution	2	3	3	3	3	3
10% Sodium bisulfite solution.....	2	2	2	2	2	4
10% Sodium chloride solution.....	2	1	1	2	2	2
10% Calcium chloride solution.....	1	1	1	2	1	2
25% Calcium chloride solution.....	1	1	1	2	2	2
Turpentine.....	2	2	2	2	2	2

As far as swelling and shrinking are concerned, it was found that all woods absorbed water from aqueous solutions, and swelled. Redwood showed the greatest effect, and oak, the slightest.

The change in physical properties, particularly the strength (brittleness) is extremely important.

It turned out that dilute 5% hydrochloric or sulfuric acid made redwood brittle. The same effect on oak was achieved with 25% hydrochloric acid; concentrated hydrochloric acid destroyed all kinds of wood. In the cold, 25% sulfuric acid did not destroy cypress or pine, but it did do so at higher temperatures. Cypress, fir, and pine were not destroyed by cold 5% nitric acid. Maple, oak, and redwood were easily attacked by 1% sodium hydroxide, while cypress and pine withstood cooking with 10% alkali, and pine was not affected even by cold 25% alkali. All types of wood were destroyed, even in the cold, by 20% sodium sulfide. Cypress, fir, and pine were the least easily attacked.

Resinous woods cannot, of course, be used as containers for organic solvents, such as alcohol. Yellow poplar or white pine are sometimes well suited for this purpose.

C. V. Gordon (13) found no appreciable decrease of the mechanical strength on six months' treatment of spruce, pine, and larch with cold 10 % and 60 % acetic acid, 10 % formic and propionic acids, 50 % methanol and a concentrated (4 %) water solution of phenol.

For further details regarding the corrosion properties of wood the reader is referred to F. Kollmann, *Technologie des Holzes und der Holzwerkstoffe*, 2nd ed., vol. I, Berlin, 1951, p. 312.

REFERENCES

1. Schwalbe, C. G., *Papier-Fabr.* **24**, 38 (1926); *Wochbl. Papierfabr.* **57**, Special No. 24A, 27 (1926).
2. Hägglund, E., and Hansen, S., *Acta Acad. Aboensis, Math. et Phys.* **3**, No. 2 (1923).
3. Hägglund, E., *Finnish Paper Timber J.* **5**, 38 (1925).
4. Hägglund, E., *Cellulosechemie* **8**, 25 (1927).
5. Smith, W. H., quoted by Schorger, A. W., *The Chemistry of Cellulose and Wood*, N. Y., 1926, p. 385.
6. Schorger, A. W., *Ind. Eng. Chem.* **9**, 556 (1917); Mahood, S. A., and Cable, D. E., *ibid.* **14**, 933 (1922); Ritter, G. J., and Fleck, L. C., *ibid.* **15**, 1055 (1923); **18**, 608 (1926).
7. Tauss, H., *Dinglers Polytech. J.* **276**, 411 (1890); Koch, W., Dissertation, Freiburg 1909; Klason, P., and Fagerlind, O., *Arkiv Kemi, Mineral. Geol.* **3**, No. 6 (1908); Bergström, H., *Papier-Fabr.* **8**, 506, 736 (1910); *ibid.* **11**, 305 (1913).
8. Sutermeister, E., *Chemistry of Pulp and Papermaking*, 2nd ed., N. Y., 1929, p. 219.
9. Franck, C., *Papier-Fabr.* **17**, 1019 (1919).
10. Bergström, H., *Papier-Fabr.* **8**, 506, 736 (1910); *ibid.* **11**, 305 (1913).
11. Robinson, C. S., *Ind. Eng. Chem.* **14**, 607 (1922).
12. Hauser, S. J., and Bahlman, C., *Chem. Met. Eng.* **18**, 528 (1918).
13. Gordon, C. V., *Chem. Abstr.* **34**, 5267 (1940); *Chem. Zentr.* **1940**, **II**, 2410.

CHAPTER XII

THE NATURAL DECOMPOSITION OF WOOD

The manner in which wood is decomposed naturally by the action of certain bacteria and fungi—a process which under some circumstances yields peat or coal—is not yet completely understood. The various opinions on this subject diverge in several important details.

Our knowledge of the humus formed by the decay of vegetable matter can be summarized as follows (1):

Humus consists of dark-colored, amorphous, natural materials formed in the ground under certain conditions by chemical and biological transformations of plant matter. Some of these materials, the humic acids, are soluble in dilute alkali, while others, known as humins, are not. There is probably a definite connection between these two classes of substances.

The manner of formation and the chemical structure of the substances which make up humus have long been objects of much investigation, and have been explained in quite different ways. The similarity between the natural humic acids and the dark-colored acid products formed by the action of acids on carbohydrates early led to the conclusion that cellulose was the precursor of the humic acids (2).

According to F. Bergius (3) cellulose is thermodynamically unstable, and the spontaneous decomposition of this substance leads to the formation of coal, with humic acids as intermediate products. At ordinary temperatures this transformation naturally requires a very long time, running up to a million years, at least. E. Erdmann (4) considered it probable that the formation of coal actually took place at elevated temperature, and hence occurred more quickly. An objection which might be raised against this viewpoint is that the occurrence of such materials as hemin and chlorophyll derivatives, spores, and amber-like resins in certain lignites and coals indicates that no very great rise in temperature has taken place.

The view that cellulose has taken part in the formation of coal has also been maintained by E. Berl and his co-workers (4 a).¹

¹ J. Marcusson (5) thinks that in the natural process of coal formation oxycelluloses are formed first from cellulose. These are then transformed into hypothetical intermediates, called "humal acids," which can be rapidly condensed to humic acids by the action of weak acid.

The lignin theory of the formation of coal, advanced by F. Fischer (6), is in complete opposition to the preceding hypothesis. According to Fischer, the humic acids are derived from the lignin component of the plants. The microorganisms attack the cellulose preferentially, thus increasing the percentage content of lignin. The methoxyl groups can then be split off hydrolytically.²

S. A. Waksman (8) has extended this theory, and emphasized particularly the great role of microorganisms in forming the humus of the soil, which is often high in nitrogen content. He believes that humus arises through a transformation of lignin-protein compounds, or "humus complexes" (9). Several soil organisms, especially the *Basidiomycetes* (8 a) and the *Hymenomycetes* (8 b), have been shown to attack both lignin and cellulose.

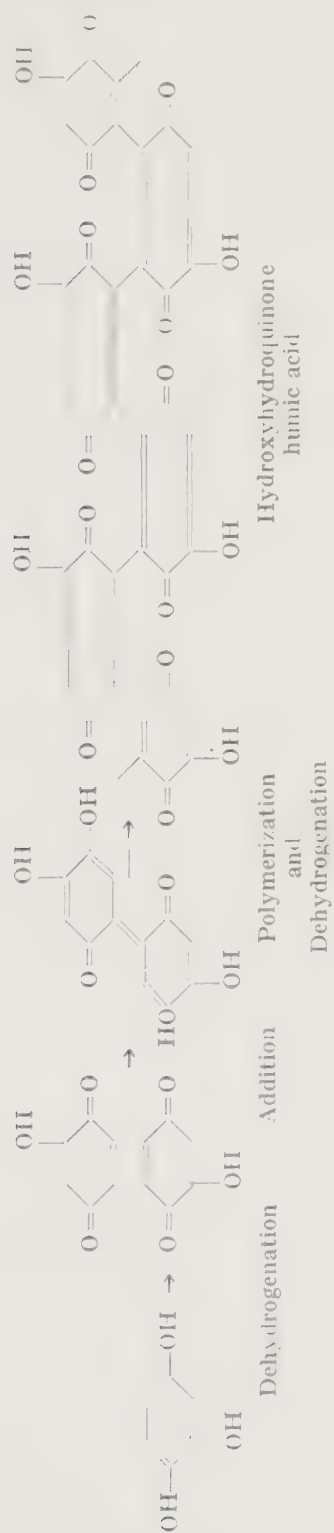
W. Eller and his co-workers (10) investigated the artificial humic acids which are formed by the action of oxygen on weakly alkaline solutions of phenols. These "phenol humic acids" are very similar to natural humic acids, and yield similar derivatives. On the other hand, the products formed by the action of acid on sugars, though similar to humic acids, differ considerably both from them and from the phenol humic acids (11). According to Eller, the humic acids are nothing but quinoid polymerization products of phenols. I. D. Sedletzki (12) has shown by X-ray analysis that both the natural and artificial humus materials are aromatic in nature. They exhibited a graphitic structure.

R. Jodl (13) compared humic acids from hydroquinone, pyrocatechol, and pyrogallol on the one hand, and from Cassel brown, peat, and bog soil on the other hand, and established the fact that there is a gradual variation from natural to artificial humic acids.

H. Erdtman (14) investigated systematically the oxidative polymerization of phenols and quinones. In his opinion, the phenols are coupled first to form diphenols, and then further, to give polyphenols. The humic acids are to be looked upon as quinoid oxidation products of the polyphenols (see the scheme, p. 555).

It has sometimes been thought that the acidic properties of the humic acids were due to acids adsorbed in the colloidal constituents of the peat, but today it is the general opinion that the acidity is due to carboxyl groups in the humic acid molecules. It should be pointed out, however, that the acidity of hydroxy quinones is in many cases as great as that of the carboxylic acids; they can, for example, be etherified with alcohols in the presence of hydrochloric acid.

² G. Agde and R. Jodl (7) have proved that X-ray diagrams of the non-bituminous constituents of lignite exhibit fundamental similarities to those of lignin (7 a) and take this as a proof of the theory (7 b).



A characteristic property of humic acids is their intense brown or black-brown color. Alkaline solutions are darker than the free acids. According to Eller's conception, the color might be explained on the basis of the quinoid structure of the humic acids. R. Pummerer and his co-workers (15) report that hydroxy derivatives of 2,5-diphenylquinone are often black-brown in color, and dissolve in alkali with a deepening of color, to give solutions whose color can scarcely be distinguished from that of phenol humic acids or of natural humic acids.

H. Erdtman (16) found that humic acids can be converted to colorless or nearly colorless leucocompounds by reduction with sodium amalgam. These leucocompounds in alkaline solution are immediately darkened by contact with the air, but are stable in acid.

The various views of the origin and constitution of the humus substances have arisen because they are not homogeneous, well-defined substances. Humuses of different origins (from peat, soil, lignite) may show marked differences. This is also true of preparations made from the same materials, but by different methods.

It is indeed probable that humus and coal can arise from cellulose as well as from lignin. Whether the process is spontaneous, or is brought about by the action of microorganisms, it is not yet possible to say. Under completely anaerobic conditions it is possible that the spontaneous transformation of plant materials to humus, envisioned particularly by F. Bergius and his co-workers, plays a leading role, especially in the last stage of coal formation. The Fischer-Schrader concept (19), which regards the humic acids as essentially aromatic materials, is closely tied up with the question of the structure of lignin. Since lignin is essentially aromatic and phenolic, it seems probable that the natural humic acids derived from lignin are polymeric hydroxy quinones of a type similar to the humic acids of Eller.

The connection of humus with lignin is shown by the investigations of H. Stach (17). He methylated humus which had been freed of alkali-soluble humic acids, and oxidized the methylated product with oxygen and cobaltic hydroxide, or with nitrobenzene. Vanillin was obtained in 5% yield; 25% of vanillin can be obtained from lignin under the same conditions.

The question as to how woods are changed by decay may be illuminated by the following figures from the work of R. E. Rose and M. W. Lisse (18).

Samples of heartwood of Douglas fir were analyzed in various stages of decay, and the results compared with the analyses of sound heartwood. The figures given in the following table are averages of three concordant values.

	Sound Heartwood %	Partially Decayed %	Completely Decayed %
Soluble in cold water.....	4.03	1.75	1.16
Soluble in hot water.....	2.23	4.19	7.77
Soluble in 1% NaOH.....	10.61	38.10	65.31
Cellulose (Cross and Bevan).....	58.96	41.66	8.47
Acid hydrolysis (Schorger).....	0.71	0.28	0.17
Pentosan (Tollens).....	7.16	6.79	2.96
Methylpentosan (Tollens).....	2.64	3.56	6.06
Methoxyl.....	3.94	5.16	7.80
Ether-extractable.....	2.71	2.05	2.72
Ash.....	0.15	0.15	0.65

Especially noteworthy is the great increase in alkali-soluble substances in the decayed wood. Rose and Lisse assume that the acidic materials formed are derived from the cellulose, since the cellulose content decreases as the acidic substances increase. The lignin is appreciably more durable than the cellulose. Particular significance is attributed to the formation of methylfurfural but this is to be regarded with some caution, since it has not been established with certainty whether or not methylpentosan occurs in wood.

F. Fischer, H. Schrader, and A. Friedrich (19) have discussed the results of Rose and Lisse, and come to the conclusion that at least half of the lignin present in the fresh wood has been transformed into humic acids on decay. It would follow from this that natural humic acids must contain methoxyl groups. This turned out to be true in the case of lignite, which had a methoxyl content of 0.91%, and of two different kinds of peat, which had methoxyl contents of 1.35-1.49% and 2.48%, respectively. Since these values are smaller than they would be if the lignin went over into humic acids with no change in its methoxyl content, it was concluded that **methoxyl groups are split off during the process of decay.**

This is of great interest in connection with the problem as to whether natural humic acids, peat, and coal are derived from cellulose, or from lignin.

Fischer and his co-workers have vigorously supported the view that lignin must be regarded as the precursor of coal. "Of the plant materials—cellulose, lignin, wax, and resin—the cellulose disappears in the course of time, chiefly by bacterial action, and coal is formed chiefly by the transformation of the lignin into humus substances, but also with additions of waxes and resins, whose relative amounts have increased by the disappearance of the cellulose."

In order to determine whether and to what extent the various constituents of wood are decomposed by fungi, it is naturally desirable to follow the entire course of the disintegration. This will also permit one to recalcu-

late the results on the basis of the original wood substance. M. W. Bray and T. M. Andrews (20) have carried out such experiments, using the fungus which is responsible for "red rot." The fungus was cultivated on mechanical pulp made from American spruce (70%) and balsam (30%).

The organisms decomposed cellulose actively, but did not attack the lignin. Only part of the methoxyl groups were split off (cf. following Table).

Bray (21) later supplemented his results. The relationship between the contents of cellulose and alkali-soluble material was plotted, and the cellulose content at various stages of decomposition by microorganisms was then read off from the curve after the alkali-soluble material had been determined.

Strain of Fungus	Duration of Expt. (months)	Yield in % of Weight of Original Wood							
		Loss by the Decay	Soluble in Cold Water	Soluble in Hot Water	Soluble in 1% NaOH	Lignin	Cellulose	Methoxyl	Copper No.
Untreated mechanical pulp.	0	0	0	1.2	10.1	29.7	60.0	5.5	4.4
4620—2.....	6	27.12	8.1	13.1	40.0	27.7	26.8	—	—
4620—2.....	12	49.5	7.5	11.1	33.4	26.7	10.9	—	—
4620—2.....	36	62.4	—	6.2	26.3	26.7	6.05	2.7	8.65
<i>Fomes roseus</i> ...	6	10.3	2.9	5.7	29.6	30.6	44.3	—	—
<i>Fomes roseus</i> ...	9	12.94	3.2	4.9	29.2	30.3	43.8	—	—
<i>Lentinus lepideus</i>	6	21.54	7.5	11.8	41.0	28.8	32.1	—	—
<i>Lentinus lepideus</i>	9	30.31	9.7	15.7	40.6	28.6	25.8	—	—
4620—1.....	6	22.2	10.8	13.7	40.8	30.7	29.0	—	—
4620—1.....	9	33.11	11.1	15.3	41.6	28.8	18.2	—	—
4620—1.....	12	38.63	9.3	13.0	38.0	28.5	16.9	—	—
<i>Peniophora tabacina</i>	6	13.5	4.8	9.0	34.9	27.7	40.5	—	—

There are also, however, certain fungi which destroy wood essentially by attacking the lignin, while leaving the cellulose intact (white rot).

R. Hartig (22) reports that *Trametes pini* belongs to this group. B. Johnsen and H. N. Lee (23) found that the action of this fungus caused the cellulose content of wood to increase by 15%, while the lignin content decreased by 30%. It is not true, however, that these fungi act on the lignin exclusively, and not at all on the cellulose, for L. F. Hawley, L. C. Fleck, and C. A. Richards (24) have shown that specimens of spruce which had been exposed to *Polyporus hirsutus*, another white rot fungus, showed decreases in the cellulose content amounting to 12.2, 12.1, and 14.7%, while the corresponding losses in weight were 9.8, 11.2, and 17.4%.

Other strains of this genus, like *P. juniperus*, dissolve the lignin of red cedar, while *P. carneus* degrades the cellulose completely. Ash was freed of lignin by the action of *P. fraxinophilus*, but the residue was not pure cellulose (25).

W. G. Campbell (26) investigated the changes in beech and ash woods which had been acted upon by *Polystictus versicolor*, and found that the pentosans and the lignin were attacked first. The lignin is presumably degraded oxidatively, with the aid of an oxidase (27).

Armillaria mellea is also considered by Campbell to be a white-rot fungus although it does not lighten the color of beech, for example. It is certainly not a red rot, since it does not cause the lignin to become alkali-soluble.

According to B. Schulze, G. Theden, and O. Vaupel (28) it is possible to investigate the changes brought about in the composition of wood by the action of fungi, by means of X-ray patterns. Fungi like *Coniophora cerebella*, *Poria vaporaria*, and *Merulius lacrimans* cause changes which result in a gradual disappearance of the patterns, since the cellulose is destroyed. The action of *Trametes pini* does not change the X-ray patterns, since this fungus attacks chiefly the lignin, which does not give a pattern.

The properties of cellulose are indeed greatly changed by wood fungi, as is evident from the experiments of Bray and Andrews, among others. The content of α - and γ -cellulose decreases greatly, while that of β -cellulose increases. The decrease in the weight of the wood is less than that of the cellulose, indicating that intermediate degradation products are formed, which are not destroyed as rapidly as they are produced.

A great decrease in the DP of the cellulose remaining after the attack of the white rot fungus *Polyporus paraganemus* upon aspen wood has also been found by E. Heuser and co-workers (28 a).

C. Wehmer (29) examined several samples of wood which had been attacked by white rot, and found in one case a humic acid content of 0.6%, while wood with red rot contained 31-36% of humic acid. According to Wehmer, this would also indicate a close connection between lignin and humus.

Wehmer's experiments also showed that isolated lignin is not attacked by wood fungi; it proved worthless as a source of carbon for the organisms. On the other hand, lignin in the cell walls is degraded by the same organisms, as also appears from the results of O. Fernández and B. Rogueiro (cf. p. 560). Evidently the lignin isolated by chemical procedures has undergone changes which make it immune to the action of fungi.

C. S. Boruff and A. M. Buswell (30) have confirmed the fact that isolated lignin is only slowly degraded under anaerobic conditions.

S. A. Waksman, and H. W. Smith (31) found that although they do not attack the lignin molecule as a whole, both anaerobic microorganisms, and to a small extent aerobic ones, have the ability to reduce the methoxyl content of the lignin.

Apparently the lignin is laid bare by the enzymes of the fungi in a form in which it can be further degraded. Wehmer is also of this opinion.

A liberation of lignin without further degradation was described by W. J. Schubert and F. F. Nord (31 a). They found that there was approximately a two-fold increase in the yield of alcohol-extractable lignin, when *Lentinus lepideus* was grown on softwood during a period of seven months. The lignin liberated by enzymatic degradation of the wood appeared to be identical with the "native lignin" of F. E. Brauns (cf. Chapter III, p. 194).

P. Kohnstamm (32) showed that the dry rot fungus (*Merulius lacrimans*) contains an enzyme which splits glycosides; this might support the view that the lignin is joined to carbohydrates by a glycosidic linkage (33).

F. Czappek (34) found that wood which had been acted upon by *M. lacrimans* contained large quantities of hadromal. Kürschner (33) stated that such wood also gave a strong odor of vanillin when it was heated, and that vanillic acid could be shown to be given off as a sublimate. The ether extract had a strong reducing action. Vanillin has also been detected as a product of wood degradation by some other tree molds (34 a).

S. A. Waksman and T. C. Cordon (35) believe that they have experimental evidence for the existence of a linkage between lignin and cellulose. Finely ground filter paper was impregnated with alkali lignin or phenol lignin, by evaporating an alkaline or alcoholic solution of the lignin-derivative, and the paper was then exposed to the action of fungi which degrade cellulose. The lignin did not protect the cellulose here, although in the wood itself the lignin does retard the degradation of the cellulose.

The experiments of T. Ploetz and of A. I. Virtanen on enzymatic and bacterial breakdown of wood and their bearing on the question of a chemical combination between lignin and cellulose have already been discussed on p. 303.

J. G. Boswell (36) investigated the disintegration products of pine wood which had been attacked by *Merulius lacrimans*, and found that only the carbohydrate portion had been affected. The action consisted in the breaking of long carbohydrate chains into shorter ones, which were soluble in alkali. It turned out that the pentosans were the most easily degraded. Oxidation also occurred along with the hydrolytic processes.

H. Pringsheim and W. Fuchs (37) also believe that the "incrusting material" is the most resistant to biological attack. They investigated the bacterial degradation of alkali lignin in ammonia solution, and found that it actually occurred. In two experiments 40% and 60% of the lignin was degraded into gaseous or water-soluble products. Of the materials precipitable with acid, one part was soluble in alcohol and had lost nearly a third of its methoxyl content.

M. Phillips (38) investigated the course of the degradation of pine-wood lignin by *Trametes pini*, and found, remarkably enough, that the sporophores contained considerable quantities of a substance which appeared to be a methoxyl-free lignin. Phillips considers it possible that the enzymatic, methoxyl-free split products of lignin might be built up again into a methoxyl-free lignin in the fungus.

The question as to whether wood which has been attacked by fungi can be used for making pulp is one of practical importance. Investigations of this matter have been made by J. D. Rue, R. N. Miller, and C. J. Humphrey (39), using balsam wood with hemlock heartrot in various stages of progress, and spruce wood infected with *Trametes pini*. Sound wood was cooked at the same time as a control. Remarkably enough, the yield of pulp was practically unchanged, and the strength of the sulfite pulp obtained was not much affected. The color of the pulp from infected wood was merely darker.

In later experiments (40), where wood was used which was not merely regionally infected, but infected in all parts, it was found that certain fungi, e.g., *Fomes pinicola*, affect the wood so that the yield of pulp decreases greatly, and the quality of the pulp is impaired.

The action of the red rot fungus *Polyporus annosus* on spruce results in an increase in the alkali-solubility of the wood, according to K. Storch (41); this may be attributed to a depolymerization of the cellulose and the lignin. The decrease in the suitability of the wood for pulp making would be connected with these changes.

D. Johansson (42) investigated the yield and quality of sulfate pulp from pine wood which had been attacked by various fungi, including *Polyporus vaporarius* or brown rot. The quality of the pulp was impaired by a decrease in strength and by a dark coloration, but the yield was not very much affected.

The reaction rate of the sulfite cooking of wood damaged by *Polystictus abietinus* is greater than that of uninfected wood, according to M. F. Martynov (43).

W. F. Holzer (44) has examined hemlock affected by heart rot (he does not give the name of the infecting organism) and tested especially the quality of the sulfite pulp. He found particularly that the pulp from infected wood was quite dark and that the α -cellulose content and especially the viscosity of the pulp were decreased, while the copper number rose, as was to be expected. The strength of the paper made from this pulp was likewise lowered, though only slightly.

An extensive investigation of the pulping characteristics of spruce wood which has been attacked by *Polyporus annosus* (a root rot fungus)

has been carried out by E. Björkman, O. Samuelson, E. Ringström, T. Bergek and E. Malm (15). Chips from different parts of the decayed trunks were mixed in different proportions with chips from sound wood, and the effect of such additions on pulp quality was investigated. Wood from the outer parts of the decayed region (so-called "aniline wood") behaved like sound wood, while wood from the inner parts, which were decayed to a higher degree, had a detrimental effect both on the yield and the quality of the pulps obtained.

C. H. Bäckström and S. Gustavsson (16) have carried out experimental pulpings of spruce and pine, which had been attacked by *Stereum sanguinolentum*. The storage of pulp wood in yards, under conditions favorable to attack by fungi, resulted in only a negligible loss after one or two years. However, if the wood is stored under such conditions for a longer time (this would probably seldom occur in practice) a considerable loss of substance occurs. After two years the spruce is so affected by *Stereum sanguinolentum* that the sulfite pulp produced from it is darkened (17). As far as the other properties are concerned, it was found that the strength of the sulfate pulp was relatively little affected by two year's storage. The sulfite pulp showed a more definite decrease in strength. It is obvious that storage for many years under unfavorable conditions, which, however, does not occur in practice, can cause great damage. T. A. Pascoe and T. C. Scheffer (18) found that unpeeled jack pine shows a much greater damage from decay than peeled wood under the same storage conditions. Storage of rough wood for 26 months (including two summers) can result in up to 10% loss of pulp yield. The physical strength of the pulp also decreased as a result of the wood decay occurring during storage. This decrease was much less in pulps from peeled wood than in those made from rough wood. Treatment of the wood with a fungicide proved ineffective. G. B. Craemer (19), in his review on wood decay, also points out that the most effective method of preventing decay during storage is to peel the logs in the woods so that they begin to dry out immediately. In this way the moisture content of the stored wood is kept below the optimum for fungus growth.

REFERENCES

1. Bibliographies in Odén, S., *Die Huminsäuren*, Leipzig, 1919, pp. 7-25; Waksman, S. A., *Humus*, 2nd ed., Baltimore, 1938; Souci, S. W., *Die Chemie des Moores*, Stuttgart, 1938.
2. Braconnot, H., *Ann. chim. phys.* [2] **12**, 172 (1819).
3. Bergius, F., *Die Anwendung hoher Drucke bei chemischen Vorgängen und die Nachbildung des Entstehungsprozesses der Steinkohle*, Halle, 1913; *Svensk Kem. Tid.* **39**, 189, 206 (1927).

1. Erdmann, E., *Jahrb. Hall. Verband (Halle)* **4**, No. 2, 249 (1934).
- 1 a. Berl, E., and Schmidt, A., *Ann.* **441**, 192 (1928); **493**, 97, 124, 135; **496**, 283 (1932); Berl, E., Schmidt, A., and Koch, H., *Angew. Chem.* **45**, 517 (1932).
5. Marcusson, J., *Z. angew. Chem.* **37**, 339 (1925); **39**, 898 (1926); **40**, 1233 (1927).
6. Fischer, F., Schrader, H., and Friedrich, A., *Ges. Abhandl. Kenntnis Kohle* **5**, 530 (1920); **6**, 133 (1921); Fischer, F., and Schrader, H., *Brennstoff-Chem.* **2**, 37 (1921).
7. Agde, G., and Jodl, R., *Braunkohle* **41**, 401 (1942).
- 7 a. Jodl, R., *Brennstoff-Chem.* **23**, 163, 178 (1942).
- 7 b. Agde, G., Schürenberg, H., and Jodl, R., *Brennstoff-Chem.* **23**, 63 (1942).
8. Waksman, S. A., and Purvis, E. R., *Soil Sci.* **34**, 43 (1932); Waksman, S. A., *Amer. J. Sci.* [5] **19**, 32 (1930); *Brennstoff-Chem.* **13**, 241 (1932).
- 8 a. Falck, R., *Ber. deutsch. bot. Ges.* **44**, 652 (1926).
- 8 b. Lindeberg, G., *Svenska Vetenskapsakad. Arkiv Botanik* **33A**, No. 10 (1946).
9. Cf. Dyck, A. W. T., and McKibbin, R. R., *Can. J. Research* **13B**, 264 (1935).
10. Eller, W., and Koch, K., *Ber.* **53**, 1469 (1920); Eller, W., *Brennstoff-Chem.* **2**, 129 (1921); *Ann.* **431**, 133 (1923); *ibid.* **442**, 160 (1925); Eller, W., and Schoppach, A., *Brennstoff-Chem.* **7**, 17 (1926).
11. Cf. also Plunguian, M., and Hibbert, H., *J. Am. Chem. Soc.* **57**, 528 (1935).
12. Sedletzki, I. D., *Soviet Geol.* **9**, No. 6, 48 (1939); *Chem. Abstr.* **34**, 6793 (1940); *Chem. Zentr.* **1940**, **I**, 3387.
13. Jodl, R., *Brennstoff-Chem.* **20**, 87 (1939).
14. Erdtman, H., *Svensk Kem. Tid.* **38**, 213 (1926); *Proc. Roy. Soc. (London)* (**A**) **143**, 177 (1933); *Ann.* **513**, 240 (1934).
15. Pummerer, R., Prell, E., and Huppmann G., *Ber.* **55**, 3113 (1922); **60**, 1442, (1927).
16. Erdtman, H., *Svensk Kem. Tid.* **38**, 207 (1926). Cf. also Zetsche, F., *Fossile Pflanzenstoffe*, in Klein's *Handbuch der Pflanzenanalyse*, vol. 3, Wien, 1932.
17. Stach, R., *Brennstoff-Chem.* **22**, 170 (1941).
18. Rose, R. E., and Lisse, M. W., *Ind. Eng. Chem.* **9**, 284 (1917).
19. Fischer, F., Schrader, H., and Friedrich, A., *Ges. Abhandl. Kenntnis Kohle* **5**, 530 (1920).
20. Bray, M. W., and Andrews, T. M., *Chem. & Met. Eng.* **18**, 528 (1918).
21. Bray, M. W., *Paper Trade J.* **78**, No. 23, 58 (1924).
22. Hartig, R., *Lehrbuch der Pflanzenkrankheiten*, 3rd. ed., Berlin, 1900, p. 173 ff.
23. Johnsen, B., and Lee, H. N., *Paper Trade J.* **76**, No. 5, 53 (1923).
24. Hawley, L. F., Fleck, L. C., and Richards, C. A., *Ind. Eng. Chem.* **20**, 504 (1928).
25. Schrenk, H. v., quoted by Schorger, A. W., *The Chemistry of Cellulose and Wood*, N. Y., 1926, p. 489.
26. Campbell, W. G., *Biochem. J.* **24**, 1235 (1930); **25**, 2023 (1931).
27. Cf. also Komarow, F., and Filimonova, G., *J. Applied Chem. U.S.S.R.* **10**, 487 (1937); *Chem. Abstr.* **31**, 5404 (1937).
28. Schulze, B., Theden, G., and Vaupel, O., *Holz Roh- u. Werkstoff* **1**, 75 (1938).
- 28 a. Heuser, E., Shema, B. F., Shockley, W., Appling, J. W., and McCoy, J. F., *Arch. Biochem.* **21**, 343 (1949).
29. Wehmer, C., *Brennstoff-Chem.* **6**, 105 (1925).
30. Boruff, C. S., and Buswell, A. M., *J. Am. Chem. Soc.* **56**, 886 (1934).
31. Waksman, S. A., and Smith, H. W., *J. Am. Chem. Soc.* **56**, 1228 (1934).
- 31 a. Schubert, W. J., and Nord, F. F., *J. Am. Chem. Soc.* **72**, 977 (1950).
32. Kohnstamm, P., *Botan. Centr. Beihefte* **10**, 90 (1901).
33. Cf. Kürschner, K., *Z. angew. Chem.* **40**, 228 (1927).

34. Czapek, F., *Ber. deut. botan. Ges.* **17**, 166 (1899).
- 34a. Fernández, O., and Rogueiro, B., *Farm. nueva* **11**, 111, 223 (1946); *Chem. Abstr.* **41**, 3293 (1947).
35. Waksman, S. A., and Cordon, T. C., *Soil Sci.* **45**, 199 (1938).
36. Boswell, J. G., *Biochem. J.* **32**, 218 (1938).
37. Pringsheim, H., and Fuchs, W., *Ber.* **56**, 2095 (1923).
38. Phillips, M., *J. Assoc. Official Agr. Chem.* **21**, 678 (1938).
39. Rue, J. D., Miller, R. N., and Humphrey, C. J., *Paper Trade J.* **78**, No. 4, 45 (1924).
40. Rue, J. D., Miller, R. N., and Humphrey, C. J., *Paper Trade J.* **78**, No. 20, 46 (1924); Kress, O., Humphrey, C. J., Richards, C. A., Bray, M. W., and Staidl, J. A., *U. S. Dept. Agr., Bull.* 1298 (1925).
41. Storch, K., *Papier-Fabr.* **35**, 485 (1937).
42. Johansson, D., *Svenska Skogsvårdsfören. Tid.* **33**, 77 (1935); Industriens Utredningsinstitut, Norrlandsutredningen, Stockholm, 1942, p. 71.
43. Martynov, M. F., *Chem. Abstr.* **35**, 5693 (1941).
44. Holzer, W. F., *Paper Trade J.* **112**, No. 19, 38 (1941).
45. Björkman, E., Samuelson, O., Ringström, E., Bergek, T., and Malm, E., *Bull. Royal School of Forestry* (Stockholm) No. 4 (1949).
46. Bäckström, C. H., and Gustavsson, S., in Björkman, E., *Meddelanden från Slatens Skogsforskningsinstitut* (Stockholm) **35**, No. 1 (1946), p. 70.
47. Cf. Lagerberg, T., *Lantbruksakad. Handl.* 1928, 66.
48. Pascoe, T. A., and Scheffer, T. C., *Paper Trade J.* **131**, No. 2, 16 (1950).
49. Craemer, G. B., *Pulp & Paper Mag. Can.* **51**, No. 4, 86 (1950).

AUTHOR INDEX

A

- ABITZ, A., see Gerngross.
- ACKER, L., see Freudenberg.
- ACREE, S. F., see Hughes.
- ADAM, K., see Freudenberg.
- ADKINS, H., FRANK, R. L., and BLOOM, E. S., Hydrogenation of alkali lignin from softwoods, 245, 376.
- Pressure hydrogenation of alkali lignin, 259.
- see Harris.
- ADLER, E., Color reactions of wood, 188, 191.
- Sugar sulfonic acids, 223, 434.
- Parallelity of acetaldehyde and vanillin formation, 234.
- Loosely bound sulfur dioxide, 429.
- Volatile aldehydes in sulfite waste liquor, 429, 430.
- Neutralization of sulfite waste liquor, 460.
- ADLER, E., and BJÖRKQVIST, K. J., Etherification of benzyl alcohols, 210, 288.
- ADLER, E., BJÖRKQVIST, K. J., and HÄGGROTH, S., Color reactions of wood, 188, 191.
- Liberation of coniferaldehyde groups in lignosulfonic acids by alkali treatment, 189, 430.
- ADLER, E., and ELLMER, L., Isolation of coniferaldehyde from wood, 184, 234.
- Combes color reaction, 192.
- Carbonyl groups in "native lignin" and lignosulfonic acid, 287.
- ADLER, E., EULER, H. V., and CEDWALL, J. O., Formation of stilbene, 235, 375.
- ADLER, E., and HÄGGROTH, S., Alkaline breakdown of coniferaldehyde groups in lignosulfonic acids, 190.
- Coniferaldehyde hydrosulfonic acid, 201.
- Carbonyl groups in lignosulfonic acid, 228.
- Alkaline cleavage of coniferaldehyde into vanillin and acetaldehyde, 233.
- Formation of vanillin from lignin, 234.
- Reddening of sulfite pulp, 455, 471.
- Fluorescence of sulfite pulp, 455, 471.
- ADLINGTON, W. E., and ROSS, J. H., Speed of soda pulping, 476, 495.
- AGDE, G., and JODL, R., Similarity of nonbituminous lignite constituents and lignin, 554.
- AGDE, G., SCHÜRENBERG, H., and JODL, R., Similarity of nonbituminous lignine constituents and lignin, 554, 563.
- AHLM, C. E., Thioglignin, 212, 372, 483.
- AHLM, C. E., and BRAUNS, F. E., Methylation of thioglycolic acid lignin, 235, 377.
- AIYAR, S. S., see Hawley.
- see Heuser.
- see Sherrard.
- AKIM, L., see Hess.
- ALFREDSSON, B., see Enkvist.
- ALVFELDT, O., see Hägglund.
- AMBRONN, H., Anisotropy of cellulose, 50, 86.
- Metal precipitation in fibers, 55.
- AMÉEN, W., see Hägglund.
- ANDERSEN, C., see Freudenberg.
- ANDERSON, A. B., Extractives from *Ponderosa* pine wood, 335.
- ANDERSON, A. B., and ERDTMAN, H., Arabinose from *Thuja plicata* heartwood, 143, 177.
- ANDERSON, A. B., and GRIPENBERG, J., Thujaplicin, 344.
- ANDERSON, A. B., and SHERRARD, E. C., Phenolic substances from the heartwood of Western red cedar, 344.
- ANDERSON, C. A., Effect of chipping on sulfite pulp strength, 450.
- ANDERSON, E., and PIGMAN, W. W., Composition of different wood tissues, 17.
- ANDERSON, R. H., and WHEELER, D. H., Tall oil, 491, 496.
- ANDERZÉN, O., and HOLMBERG, B., Alkali lignin, 481.
- ANDERZÉN, O., see Holmberg.
- ANDREWS, T. M., see Bray.
- ANT-WUORINEN, O., Hydrolysis of different celluloses with dilute sulfuric acid, 97.
- Wood saccharification with dilute sulfurous acid, 397.
- APPLING, J. W., see Heuser.
- see Wise.
- ARIES, R. S., Comparison of pulp qualities, 438.
- Use of lignin for soil improvement, 464.
- Stability of bisulfite solutions, 499, 504.
- see Katzen.
- ARMBRUSTER, F. K., see Kobe.
- ARNOLD, G. C., SIMMONDS, F. A., and CURRAN, C. E., Alkali consumption in bleaching, 517, 528.
- Influence of alkali extraction on strength properties, 526, 528.
- ARNOLD, S., see Hägglund.
- ARNOULD, J. E., Wood saccharification with concentrated sulfuric acid, 400.

- ARONOVSKY, S. I., Pulping with sodium sulfite, 488, 496.
- ARONOVSKY, S. I., and GORTNER, R. A., Treatment of aspen sawdust with water under pressure, 105.
- Extraction of lignin with alcohol-benzene mixtures, 194, 370.
- Pulping with sodium sulfite, 488, 496.
- ARONOVSKY, S. I., see Reid.
- ARONOWSKY, A., see Pringsheim.
- ARRHENIUS, O., Variation of the fat content in different trees, 334.
- ARRHENIUS, S., Effect of sodium hydroxide and sodium sulfide solutions in equivalent concentration on wood pulping, 476, 477, 495.
- ASCHAN, B., see Heuser.
- ASCHAN, O., Constituents of turpentine oils, 333.
- Solubility of wood resins, 336.
- Reddening of sulfite pulp, 454.
- Sulfite turpentine, 457.
- Formation of acetic acid in wood distillation, 534.
- ASPLUND, A. J. A., Defibration of wood, 105.
- ASSAF, A. G., HAAS, R. H., and PURVES, C. B., Reaction between cellulose and thallium ethylate, 60.
- ATCHINSON, R. L., Polymolecularity of cellulose, 123, 174.
- ATTERER, M., see Schmidt.
- AULIN-ERDTMAN, G., Bromination of cerulignol, 281, 381.
- Spectrochemistry of lignin, 210, 292, 314, 318, 371, 382.
- Constitution of dehydro-diisoeugenol, 313.
- Free phenolic hydroxyls in lignosulfonic acid, 200, 286, 371.
- AULIN-ERDTMAN, G., BJÖRKMAN, A., ERDTMAN, H., and HÄGGLUND, S. E., Sulfonation of a cyclic semiacetal, 201.
- Ultraviolet absorption of lignosulfonic acids, 210, 371.
- 2,4-Dinitrophenylhydrazones of lignosulfonic acids, 288, 371.
- AULIN-ERDTMAN, G., and ERDTMAN, H., Ultraviolet absorption of lignans, 343.
- Synthesis of pinosylvins, 344, 389.
- AULIN-ERDTMAN, G., see Hägglund.
- AUSTERWEIL, G., and LEMAY, L., Purification of crude cymene, 457, 472.
- AUSTERWEIL, G., and ROTH, J., Turpentine oil and colophony in wood, 333.
- terium and hydroxyl groups in cellulose 60, 166.
- BÄCKSTRÖM, C. H., and GUSTAVSSON, S., Sulfite pulping of decayed wood, 562.
- BAEYER, A., and VILLIGER, V., Reaction between triphenylcarbinol and sodium bisulfite, 202.
- BAHLMAN, C., see Hauser.
- BAILEY, A. J., Butanol lignin, 239, 240.
- Volatile substances from hydrochloric acid treatment of butanol lignin, 240, 375.
- Molecular size of lignin, 295.
- Constituents of middle lamella, 305.
- BAILEY, A. J., and BROOKS, H. M., Electrolytic oxidation of butanol lignin, 240.
- BAILEY, A. J., see Pearl.
- BAILEY, I. W., see Kerr.
- BAIRD, F. K., see Billington.
- BAMFORD, K. F., see Campbell.
- BANDERET, A., and RÄNBY, B. G., Presence of highly alkali sensitive linkages in cellulose, 91.
- BARBOUR, J. H., see Ritter.
- BARD, J. W., Bleachability of soda pulps, 488, 495.
- BARILOT, E., Carbonization of wood, 533.
- BARNES, F., Extractives from soft-wood, 336.
- BARRAUD, M., see Dupont.
- BARRE, H. C., and BLONDEL, C. M., Pulping with nitric acid, 503, 505.
- BARRY, A. J., see Peterson.
- BARSHA, J., and HIBBERT, H., Methylation of sulfite pulps, 122.
- BARTHOLME, M., see Müller.
- BASBERG, A., Reaction time in soda pulping, 476, 495.
- BATEMAN, E., see Sherrard.
- BATH, F., see Ellis.
- BÄTTISTA, O. A., and COPPICK, S., Mild hydrolysis of cellulose, 81.
- BAUER, R., see Voss.
- BAULE, B., see Kratky.
- BAUMHAUER, E. H. v., Incrustation theory, 297.
- BEADLE, C., see Cross.
- BEARSE, N. J., see Frankevičs.
- BÉCHAMP, A., Hydrochloric acid lignin, 264, 379.
- Saccharification of cellulose, 402.
- BECK, M. M., see Cundy.
- BECKER, E., see König.
- see Schwalbe.
- BECKMANN, E., LIESCHE, O., and LEHMANN, F., Lignin formation in relation to plant growth, 321.
- BEGLINGER, E., see Harris.
- see Sherrard.

BADENHUIZEN, N. P., see Meyer.

BADGER, R. M., see Blaker.

BADGLEY, W., FRILETTE, V. J., and MARK, H., Reaction between deu-

- BELL, A., HAWKINS, W. L., WRIGHT, G. F., and HIBBERT, H., Syringaldehyde from birch lignosulfonic acid, 231, 374.
- BELL, D. J., Methylation of cellulose, 122.
- BELZ, W., see Freudenberg.
- BENDER, R., see Grassmann.
- BENGTSOON, E., see Sandqvist.
- BENOIST, S., see Bertrand.
- BENSON, H. K., and JONES, F. M., Tannin content of different woods, 344.
- BENSON, H. K., see Carpenter.
- see Hiester.
- see Pearl.
- see Pedersen.
- see Skewes.
- BENTE, F., Chemical linkage between wood constituents, 38.
- BERG, G. A. and HOLMBERG, B., Mechanism of alcohol lignin formation, 202, 239, 253, 260, 371.
- BERG, J. C. VAN DEN, see Böeseken.
- BERGEK, T., Aging of alkali cellulose, 91.
- BERGEK, T., GUSTAVSSON, S., and LINDVALL, E., Alkaline cleavage of oxycellulose, 85.
- Stability of oxycellulose in alkali, 520, 529.
- BERGEK, T., see Björkman.
- see Hägglund.
- BERGER, H. W., see Grondal.
- BERGH, Å., see Klason.
- BERGIUS, F., Rheinau process, 404, 413.
- Humic acids, 553.
- BERGIUS, F., and ERASMUS, P., Coal formation, 104.
- BERGIUS, F., FÄRBER, E., and JELLINEK, O., Rheinau process, 404, 413.
- BERGIUS, F., KOCH, FR., and FÄRBER, E., Plastics from wood saccharification lignin, 405, 413.
- BERGIUS, F., and SPECHT, H., Heating of cellulose in water, 103.
- BERGIUS, F., see Hägglund.
- BERGMANN, M., and MACHEMER, H., End-group determination in cellulose, 45.
- BERGSON, C. R., Fermentation of sulfite waste liquor, 459.
- BERGSTROM, H., Resin content of turpentine oils, 333.
- Composition of turpentine oil, 333.
- Fatty acids in pine, 335.
- Formation of methyl alcohol during sulfite pulping, 457.
- Volatile by-products from sulfate pulping, 491, 496.
- Tall oil, 492.
- Composition of the gas liberated on wood distillation, 535.
- Changes in wet chips on storage, 538.
- Extraction of wood with hot water, 550, 552.
- BERGSTROM, H., and CEDERQUIST, K., Extractability of wood cellulose, 300.
- BERGSTROM, H., CEDERQUIST, K., and TROBECK, K. G., Pressure heating of wood with lime, 546.
- Digestion of wood with tars and phenols, 546, 547.
- BERGSTROM, H., and FAGERLIND, O., Turpentine oil from root wood extract, 333.
- BERGSTROM, H., and TROBECK, K. G., Volatile by-products from sulfate pulping 491, 496.
- BERGSTROM, H., and WESSLÉN, G., Thermal decomposition of wood, 531, 539.
- BERGSTROM, C. B., see Harris.
- BERKMAN, S., BÖHM, J., and ZOCHER, H., Intermicellar spaces, 55.
- BERL, E., and SCHMIDT, A., Formation of coal, 553, 563.
- BERL, E., SCHMIDT, A., and KOCH, H., Formation of coal, 553, 563.
- BERLING, K., see Schwalbe.
- BERNOLD, E., see Ruzicka.
- BERTRAND, G., Occurrence of mannan in wood, 144.
- BERTRAND, G., and BENOIST, S., Cello-triose, 43.
- BETTELHEIM, L., see Fuchs.
- BEVAN, E. J., see Cross.
- BÉZARD, A. V., see Wacek.
- BICKFORD, W. G., see Fisher.
- BILDT, O., Weak pulp from crushed wood, 450, 471.
- BILLINGTON, P. A., SUMMONDS, F. A., and BAIRD, P. K., Determination of lignin, 327, 386.
- BIRCH, A. J., and LIONS, F., Gmelinol, 341, 388.
- BIRCHARD, W. H., Hydrogen ion concentration in sulfite cooking liquor, 423.
- BIRD, C. D., see Ritter.
- BIRTWELL, C., CLIBBENS, D. A., and GEAKE, A., Hydrocellulose, 78, 169.
- BJÖRKMAN, A., Hydrogenation of sulfite waste liquor, 467.
- see Aulin-Erdtman.
- BJÖRKMAN, C. B., Determination of the pulping degree, 436, 469.
- see Hägglund.
- BJÖRKMAN, E., SAMUELSON, O., BERGEK, T., and MALM, E., Pulping of decayed wood, 562, 564.
- BJÖRKQVIST, K. J., see Adler.
- BLAINE, R. L., see Browen.

- BLAKER, R. H., BADGER, R. M., and NOYERS, R. M., Polymolecularity of nitrated cellulose, 123.
- BLANCO, G. W., see Sherrard.
- BLAXALL, F. R., see Macfadyen.
- BLECKMANN, N. C., see Kratzl.
- BLOMQUIST, G., see Freudenberg.
- BLONDEL, C. M., see Barre.
- BLOOM, E. S., see Adkins.
- BLOOM, T., and JAHN, E. C., Pulping with ethanolamine, 133, 176.
- BLUMRICH, K., see Wohl.
- BOCK, H., see Schneider.
- BODDING-WIGER, B., see Karrer.
- BOEDEKER, E., see Heuser.
- BOEDEKER, H., see Hägglund.
- BOEDTKER, E., Composition of sulfite turpentine, 457.
- BÖESEKEN, F., BERG, J. C. VAN DEN, and KERSTJENS, A. H., Acetolytic breakdown of cellulose, 42, 162.
- BÖHM, J., see Berkman.
- BOER, J. H. DE, Strength of the main valence chain of cellulose, 116, 173.
- BÖTTGER, S., see Helferich.
- BOHUNEK, H., see Hoch.
- BOLZ, F., see Freudenberg.
- see Noll.
- BOND, W. J., GODDARD, J. G., and WRIGHT, G. F., Absence of piperonyl groups in *Sassafras* lignin, 292, 382.
- BOOYS, J. DE, see Hermans.
- BOPPEL, H., see Freudenberg.
- see Plankenhorn.
- BORGHENSAM, E., Distillation of wood, 533.
- BORLEW, P. B., and PASCOE, T. A., Consumption of sulfide during sulfate cooking, 480, 495.
- BORODINA, O., Molecular weight of lignosulfonic acids, 223.
- BORSCHÉ, W., and NIEMANN, J., Podophyllotoxin, 343, 388.
- BORUFF, C. S., and BUSWELL, A. M., Decomposition of isolated lignin by microorganisms, 559.
- BOSWELL, J. G., Decomposition of pine wood by *Merulius lacrimans*, 560.
- BOWER, R. S., see Fisher.
- BRACONNOT, H., Saccharification of cellulose and wood, 37, 263, 400.
- Humic acids, 553, 562.
- BRADLEY, L., and MCKEEFE, E. P., Pulping of pine heartwood according to the Graham method, 447, 470.
- BRADLEY, L., see McKeeffe.
- BRAGG, W. H., Atomic diameter of carbon and oxygen, 50.
- BRANDES, E., see Fries.
- BRANDT, C. W., and NEUBAUER, L. G., Ferruginol, 338, 388.
- BRATT, L. C., see Hägglund.
- BRAUN, E., Shape of lignin molecules, 296, 382.
- see Freudenberg.
- BRAUNS, F. E., Polysaccharide containing 72.6 % galactose from *Picea mariana*, 153.
- Phloroglucinol reaction of "native lignin", 189.
- Color reaction of "native lignin" with hydrochloric acid, 191, 288.
- "Native lignin" from black spruce, 194, 483.
- "Native lignin" from Western Hemlock, 195.
- Ethers of alkali lignin, 260.
- Methylation of "native lignin", 284.
- Carbonyl groups in "native lignin", 287.
- Conidendrin from Western Hemlock, 342.
- Splitting of methoxyl groups on bromination of lignin, 512, 528.
- BRAUNS, F. E., and BROWN, D. S., Sulfite cooking of methylated wood, 212.
- Conversion of lignosulfonic acid from insoluble to soluble state, 218.
- BRAUNS, F. E., and BUCHANAN, M. A., Acetic acid lignin, 251.
- Reaction of isolated lignins with thioglycolic acid, 253.
- BRAUNS, F. E., and GRIMES, W. S., Alkali lignin, 256, 378.
- Alkali consumption during alkaline pulping, 476.
- BRAUNS, F. E., and HIBBERT, H., Composition of lignin, 239, 283.
- BRAUNS, F. E., and LANE, W. H., Reaction of "native lignin" with thiophenol, 247.
- BRAUNS, F. E., and LEWIS, H. F., Alkali lignin from red wood bark, 257.
- BRAUNS, F. E., and YIRAK, J. J., Insolubility of lignin in methylated wood on alkaline pulping, 259.
- Chemical linkage between lignin and carbohydrates in spruce wood, 302.
- BRAUNS, F. E., see Ahlm.
- see Buchanan.
- see Buckland.
- see Gray.
- see Hibbert.
- see Lewis.
- see Marshall.
- BRAUNS, O., Evaporation of sulfite waste liquor, 429, 468.
- BRAWN, J. S., HEDDLE, R. D., and GARDNER, J. A. F., Alcoholysis of wood, 241, 376.
- BRAY, M. W., Sulfite pulping of hardwoods, 448.

- Red rot, 558.
- BRAY, M. W., and ANDREWS, T. M., Red rot, 558.
- BRAY, M. W., and CURRAN, C. E., Effect of spring and summer wood content on pulp quality, 443, 470.
- Kinetics of alkaline pulping, 476, 495.
- BRAY, M. W., and EASTWOOD, P. R., Pulping with sodium sulfite, 499, 504.
- BRAY, M. W., and MARTIN, J. S., Sulfate pulping of hardwoods, 490.
- High-yield sulfate and soda semi-chemical pulping, 499, 504.
- BRAY, M. W., MARTIN, J. S., and CARPENTER, L. A., Effect of sulfur in soda pulping, 488, 496.
- BRAY, M. W., MARTIN, J. S., and SCHWARTZ, S. L., Kinetics of alkaline pulping, 476, 495.
- BRAY, M. W. and SINGER, S., Addition of sulfite or thiosulfite to soda cooking liquor, 476, 495.
- BRAY, M. W., see Chidester.
- see Kress.
- see Martin.
- see Peterson.
- see Schwartz.
- see Wells.
- BREDÉE, H. L., Xanthation of cellulose, 64.
- BRELAZ, G. L., see Pictet.
- BRENNAN, J. E., MacMAHON, J. D., and VINCENT, G. P., Chlorite activation with chlorine and hypochlorite, 523, 530.
- BRENNER, F. C., FRILETTE, V. J., and MARK, H., Recrystallization of amorphous cellulose, 61.
- BREWER, C. P., COOKE, L. M., and HIBBERT, H., Hydrol lignin, 262.
- BRICKMAN, L., HAWKINS, W. L., and HIBBERT, H., Alcoholysis of different woods, 242, 376.
- BRICKMAN, L., PYLE, J. J., HAWKINS, W. L., and HIBBERT, H., Alcoholysis of different woods, 242, 376.
- BRIGGS, J. F., see Cross.
- BRIGGS, L. H., and FRIEBERG, A. G., Isoolivil, 341, 388.
- BRIGGS, L. H., PEAK, D. A., and WOOLLOXALL, J. L. D., Matairesinol, 340, 388.
- BRINK, D. L., HOSSFELD, R. L., and SANDSTROM, W. M., Low-molecular products from aspen wood on hydro-sulfide cooking, 488.
- BRINTZINGER, H., Determination of the molecular weight by dialysis, 223.
- BRODTKORB, T., see Ost.
- BROOKBANK, E. B., Catalytic hydrogenation of Meadol, 258, 378.
- Utilization of soda lignin, 260, 378.
- see Lewis.
- BROOKS, H. M., see Bailey.
- BROWEN, J. W., and BLAINE, R. L., Adsorption of gases by fibers, 55, 165.
- BROWN, B. E., see Phillips.
- BROWNE, C. A., JR., and TOLLENS, B., Araban, 159, 179.
- BROWNING, B. L., see Pigman.
- see Stillings.
- BRUCH, E., see Freudenberg.
- BRÜDA, B., see Friedrich.
- BRUNES, B., SAMUELSON, O., and ULFSPARRE, S., Evaporation of sulfite waste liquor, 429, 468.
- BRUUN, J., Reaction velocity of pulping with sodium hydroxide, 476, 495.
- BRYDE, O., Pulping with ammonium bisulfite, 424.
- BRYDE, O., and RÅNBY, B. G., Molecular weight of native wood cellulose, 74, 124.
- BUCHANAN, M. A., BRAUNS, F. E., and LEAF, R. L., JR., "Native lignin" from aspen, 195.
- BUCHANAN, M. A., LOLLAR, R. M., and NIEMEYER, D. D., Tanning properties of lignosulfonates, 465.
- BUCHANAN, M. A., see Brauns.
- see Coleman.
- see Isenberg.
- see Lewis.
- BUCHERER, H., Sulfonation of lignin, 199.
- BUCKLAND, I. K., BRAUNS, F. E., and HIBBERT, H., Sulfite cooking of methylated wood, 212.
- Phenol lignin from spruce wood, 246.
- BUCKLAND, I. K., see Hibbert.
- BUDNIKOFF, P. P., Recovery of sulfuric acid in wood saccharification, 402, 413.
- BÜHLER, F. A., Determination of cellulose, 126.
- Phenol lignin, 246.
- BÜTTNER, G., and WISLIGENUS, H., Distillation of wood with superheated steam, 537, 539.
- BÜTTNER, G., see Wislicenus.
- BUGGE, G., Wood distillation, 531, 539.
- BUJEWSKOI, A., Hydrolysis of hydro-cellulose, 81.
- Hydrolysis of cellulose, 97.
- BUJEWSKOI, A., and WEDENEJEW, W., Hydrolysis of cellulose, 97, 171.
- BUMANN, I., see Freudenberg.
- BUNBURY, H. M., Wood distillation, 531.
- BURCH, B. G. N., SHAW, A. C., and NICHOLLS, R. V. V., Phytosterol in Canadian tall oil, 492, 496.
- BURGESS, H., see Watt.

- BURGSTALLER, F., and SONDERHOFF, R.,
Influence of bleaching on sizing, 526,
530.
- BUSCH, H., see Hägglund.
— see Knoevenagel.
- BUSWELL, A. M., DOWNING, F. R., and
RODEBUSH, W. H., Hydrogen bonds
in cellulose, 54, 165.
— see Boruff.
- BUTTER, G., see Voss.
- BYMAN, L., Tall oil, 492.
- BYWATER, R. A. S., HAWORTH, W. N.,
HIRST, E. L., and PEAT, S., Esparto
xylan and arabinose, 142, 177.
- C
- CABLE, D. E., see Mahood.
- CADENBACH, G., see Fredenhagen.
- CALHOUN, J. M., see Maass.
- CALKINS, C. R., see Pigman.
- CAMERON, F. K., see Wan Chen.
- CAMERON, W. G., and MORTON, T. H.,
Cross-linking in cellulose, 49.
- CAMPBELL, J., and ROLLESTON, L. O.,
Chlorination with gaseous chlorine,
515, 528.
- CAMPBELL, W. B., and MAASS, O., Hydro-
gen ion concentration of bisulfite
cooking liquors, 423.
- CAMPBELL, W. G., Methyl and ethyl
lignin, 239.
— Decomposition of beech and ash wood
by *Polystictus versicolor*, 559.
- CAMPBELL, W. G., and BAMFORD, K. F.,
Determination of lignin, 327, 386.
- CAMPBELL, W. G., and MCGOWAN, J. C.,
Chlorine-sodium sulfite reaction of
hardwoods, 193.
- CAMPBELL, W. G., see Hirst.
- CAMPBELL, W. P., see Fieser.
- CANDLIN, E. J., and SCHRYVER, S. B.,
Pectin content of wood, 135.
- CANNON, J. J. R., see Maass.
- CANTOR, G. M., see Hurd.
- CARLSSON, G. E., see Hägglund.
- CARMODY, W. R., and MEARS, J. S.,
Kinetics of chlorination of pulp, 508, 511,
512.
— Chlorine consumption in bleaching,
514.
- CARNAP, A., see Husemann.
- CAROLLES, B. DE, Effect of sulfuric acid
on cellulose, 86.
- CARPENTER, J. S., and BENSON, H. K.,
Nitration of lignosulfonic acid, 227.
- CARPENTER, L. A., see Bray.
- CARPENTER, P., see Escourrou.
- CASCIANI, F., and STORIN, G. K., pH in
hypochlorite bleaching, 520, 529.
— Influence of hypochlorite bleaching
on strength properties, 526, 529.
- CASPARIS, P., Cobalt rhodanide reaction
of wood, 193, 370.
— Lignin formation, 320.
- CATALDI, P., Chlorine-alkali pulping, 502,
505.
- CEDERQVIST, K., see Bergström.
- CEDWALL, J. O., see Adler.
- CENTOLA, G., State of cellulose in solu-
tions, 64.
- CHALMOT, G. DE, Pentosan content of
different woods, 159.
- CHAMPETIER, G., and BONNET, J., Cellu-
lose sulfuric acid ester, 86.
- CHAMPETIER, G., and VIALARD, R.,
Reaction between deuterium and hy-
droxyl groups in cellulose, 60, 166.
- CHAPMAN, P. E., see Vilbrandt.
- CHARBONNIER, H. Y., Butanol lignin, 240.
— see Heuser.
- CHARLTON, W., HAWORTH, W. N., and
PEATS, S., Constitution of cellobiose,
43, 163.
- CHESLEY, K. C., see Smith.
- CHIDESTER, G. H., Semichemical pulp,
499, 500, 504, 505.
- CHIDESTER, G. H., BRAY, M. W., and
CURRAN, C. E., Effect of spring and
summer wood content on pulp quality,
443, 470.
- CHIDESTER, G. H., and MCGOVERN, J. N.,
Pulping with sulfurous acid, 437, 469.
— Effect of spring and summer wood
content on pulp quality, 443, 470.
— Neutral sulfite pulping, 499, 504.
- CHIDESTER, G. H., MCGOVERN, J. N., and
McNAUGHTON, C. C., Relation of
spring and summer wood content to
pulp quality, 443, 470.
- CHIDESTER, G. H., see Curran.
— see Heritage.
- CHILSON, W. A., Multistage bleach, 521.
— Sulfur dioxide treatment of bleached
pulp, 521, 529.
- CHORLEY, J. C., and RAMSAY, W., Dry
distillation of cellulose, 107.
— Dry distillation of wood, 531, 539.
- CHRISTENSEN, C. M., see Veldhuis.
- CHRISTIANSEN, C., Alkali consumption
during alkaline pulping 476, 494.
— Changes in alkalinity during alkaline
pulping, 477.
- CLARK, J. d'A., Keebra process, 498, 499,
504.
- CLARK, T., Chlorination at elevated tem-
peratures, 512, 528.
— Two-stage hypochlorite bleach, 521,
528.
- CLASSEN, A., Wood saccharification with
sulfurous acid, 392.
— Wood saccharification with concen-
trated sulfuric acid, 400.

- CLAUSEN, P., Bacterial formation of methane from cellulose, 110.
- CLAYTON, J., see Hutchinson.
- CLEVE-V. EULER, A., Incrusting material in wood, 181, 368.
- Formation of lignin, 320.
- Determination of lignin, 327, 386.
- Extraction of wood with alcohol-benzene, 339.
- CLIBBENS, D. A., and RIDGE, B. P., Hydrocellulose, 81.
- Oxidation of cellulose, 83.
- Formation of oxycellulose, 520, 529.
- CLIBBENS, D. A., see Birtwell.
- COBLEY, T. H., Pulping with sodium sulfite, 499, 504.
- COHEN, W. E., and HARRIS, E. E., Determination of lignin, 327, 386.
- COHEN, W. E., see Stamm.
- COHN, R., see Neuberg.
- COHOE, W. P., Wood saccharification, 394.
- COLEMAN, G. H., BUCHANAN, M. A., and PAUL, P. T., Reversion of sugar solutions, 99, 171.
- COMBES, R., Color reaction of wood, 192.
- CONNER, W. P., Molecular size of lignin, 296.
- CONRAD, C., see Nelson.
- CONSRUCH, K., see Husemann.
- COOKE, L. M., MCCARTHY, J. L., and HIBBERT, H., Pressure hydrogenation of ethanol lignin, 245.
- see Brewer.
- COPPICK, S., Degree of polymerization of cellulose, 124.
- see Battista.
- CORDON, T. C., see Waksman.
- CORRENS, E., Refining of sulfite pulp, 489.
- see Dolmetsch.
- COSTER, N. W., and THIEME, R. I., Chlorination at elevated temperature, 512, 528.
- Solubility of chlorination products in water, 516.
- Effect of chlorination on cellulose, 525, 528.
- COUNCLER, C., Determination of cellulose, 126.
- COVELLI, E., Color reactions of wood, 183.
- COVEY, A. J., see Tasman.
- COX, R. F. B., 3,5-Dimethoxystilbene, 344.
- CRÆMER, G. B., Pulping of decayed wood, 562.
- CRAMER, A. B., HUNTER, M. J., and HIBBERT, H., Water soluble products from wood alcoholysis 241, 376.
- CRAMER, A. B., see Hunter.
- CREIGHTON, R. H. J., GIBBS, R. D., and HIBBERT, H., Nitrobenzene oxidation of lignin, 214.
- CREIGHTON, R. H. J., MCCARTHY, J. L., and HIBBERT, H., Oxidation of maple lignin, 280.
- CRIEGEE, R., Determination of double bonds, 289, 382.
- CROCKER, E. C., Specificity of the phloroglucinol reaction, 187.
- Color reaction of lignin with ferric ferricyanide, 190, 369.
- Mäule reaction, 193.
- CROCKIN, J. M., see Vilbrandt.
- CROSS, C. F., Linkage between lignin and carbohydrates, 297.
- Incrustation theory, 297.
- Pulping with sodium sulfite, 498.
- CROSS, C. F., and BEVAN, E. J., Wood saccharification, 410, 413.
- Determination of cellulose, 125, 126.
- Furfuroids, 161.
- Color reactions of wood, 184, 185, 368.
- Color reaction of lignin with ferric ferricyanide, 190.
- Color reaction of wood with chlorine-sodium sulfite, 190, 369.
- Pulping with nitric acid, 126, 503.
- CROSS, C. F., BEVAN, E. J., and BEADLE, C., Furfuroids in wood, 161, 180.
- CROSS, C. F., BEVAN, E. J., and BRIGGS, J. F., Indirect determination of lignin, 332.
- Color reactions of wood, 184, 185, 368.
- CROSS, C. F., BEVAN, E. J., and ISAAC, J. F. V., Formation of acetic acid on caustic fusion of carbohydrates, 542.
- CROSS, C. F., BEVAN, E. J., and SMITH, C., Furfuroids in straw and esparto, 161, 180.
- CROSS, C. F., and ENGELSTAD, A., Pulping with sulfurous acid, 437, 469.
- CROSS, W. E., Acetyl groups in wood, 349, 389.
- Acetic and formic acids in wood.
- Acetic and formic acids in wood hydrolyzates, 456.
- CROSS, W. E., and TOLLENS, B., Liberation of acetic acid on wood hydrolysis, 357.
- CUNNINGHAM, G. M., see Taylor.
- CUNDY, P. F., and BECK, M. M., Determination of α -cellulose, 134.
- CURRAN, C. E., Relation of spring and summer wood content to pulp quality, 443, 470.
- Pulping with sodium sulfite, 499, 504.
- CURRAN, C. E., MONSSON, W. H., and CHIDESTER, G. H., High-yield acid sulfite pulping, 499, 504.
- CURRAN, C. E., see Arnold.
- see Bray.

- see Chidester.
 - see Heritage.
 - see Martin.
 - CZAPEK, F., Color reactions of wood, 183.
 - Colorimetric determination of lignin, 184.
 - Phloroglucinol reaction of wood, 187.
 - Linkage between lignin and carbohydrates, 297.
 - Tannin content of willow bark, 344, 389.
 - Hadromal in wood attacked by *Merulius lacrimans*, 560.
- D
- D'ADDIECO, A. A., see Wise.
 - DÄUBNER, H., see Kratzl.
 - DÄUBNER-RETENBACHER, H., see Wacek.
 - DAHLÉN, A., Oil content of linden wood, 335.
 - DAMMEL, W., see Heuser.
 - DANGEVILLIERS, E. S., Wood saccharification with concentrated hydrochloric acid, 402.
 - DANIELS, H. S., and MCCARTHY, J. L., Butyric acid fermentation of sulfite waste liquor, 464.
 - DANILOW, S. N., and PASTUCHOW, P. T., Acetolysis of cellulose, 43.
 - DARBOVEN, J. W., Wood saccharification with concentrated hydrochloric acid in organic solvents, 410.
 - DAUBE, W., Elementary composition and ash content of sapwood and heartwood, 37.
 - Chemical composition of wood ash, 348.
 - DAUMILLER, G., see Staudinger.
 - DAUR, W., see Küster.
 - DAVID, E., see Wacek.
 - DAVIDSON, G. F., Oxidation of cellulose, 83.
 - Oxidation of cellulose with periodic acid, 83.
 - Stability of oxycellulose in alkali, 520, 529.
 - DAVIES, A. E., see Menzies.
 - DEAN, A. L., and TOWER, G. E., Determination of cellulose, 125.
 - DEBYE, P., Light scattering of high-molecular substances, 75.
 - DEBYE, P., and SCHERRER, P., X-ray examination of cellulose, 121.
 - DEDICHEN, H., see Halse.
 - DE LEEUW, A. J., see Hermans.
 - DEMUTH, R. v., Wood saccharification with dilute acids, 392, 395, 411.
 - DENHAM, W. S., and WOODHOUSE, H., Methylation of cellulose, 43.
 - DESCH, H. E., Physical properties of wood, 36.
 - DESMAROUX, J., and MATHIEU, M., State of cellulose in solutions, 64.
 - D'IANNI, J., see Harris.
 - DICKERMAN, G. K., see Saeman.
 - see McGovern.
 - DICKEY, E. E., and WOLFROM, M. L., Acetolysis of cellulose, 44.
 - DIECKMANN, R., Addition of sulfite waste liquor to fresh cooking liquor, 433, 469.
 - DIETRICH, G., see Freudenberg.
 - DIETRICH, K. R., see Sabalitschka.
 - DILLENIUS, H., Cross-linked cellulose, 49, 164.
 - DIMROTH, O., Determination of double bonds, 289, 382.
 - DITTMER, M., Composition of sulfate soap, 335.
 - Tall oil, 492.
 - DIWALD, J., see Friedrich.
 - DMOCHOWSKY, R., see Tollens.
 - DOBLAND, R. M., HAWKINS, W., L., and HIBBERT, H., Solubility of formic and acetic acid lignins in bisulfite solution, 240, 375.
 - DODGE, F. D., Cinnamaldehyde hydro-sulfonic acid, 201, 371.
 - DÖRR, R. E., Degree of polymerization of rayon, 68.
 - Extraction of pentosans from straw, 141.
 - Prehydrolysis and alkaline pulping, 475.
 - DOHSE, H., Structure of the cellulose molecule, 50, 164.
 - DOLMETSCH, H., Fine structure of spruce wood fiber, 362.
 - DOLMETSCH, H., FRANZ, E., and CORRENS, E., Construction of the cell wall, 359, 360, 361, 452, 471.
 - DOLMETSCH, H., and REINECKE, F., Polymolecularity of wood pulps, 123, 453.
 - DORE, W. H., Acetyl content of the xylans, 105.
 - Mannan content of different woods, 148.
 - Galactan content of different woods, 151.
 - Acetyl groups in wood, 349.
 - see Sponsler.
 - DORÉE, C., and HALL, L., Reaction products of lignosulfonic acid and amines, 220, 372.
 - Addition of bromine to lignosulfonic acid, 226.
 - Nitration of lignosulfonic acid, 227.
 - Pulping with sulfurous acid, 437.
 - DOTY, P. M., see Stein.
 - DOWNING, F. R., see Buswell.
 - DREHER, E., see Staudinger.

- DREWSSEN, V. B., Dry distillation of black liquor, 493, 497.
 — Keebra-process, 498, 499, 504.
 DREYFUS, H., Wood saccharification with hydrochloric acid, 410, 413.
 DREYFUSS, P., Olivil, 322, 385.
 — see Vanzetti.
 DRYDEN, E. C., see Reid.
 DÜRR, W., see Freudenberg.
 DUKELSKY, S., Color reactions of wood, 183.
 DUPONT, G., and BARRAND, M., Terpenes from *Pinus palustris*, 334.
 DU RIETZ, C., Kinetics of sulfite pulping, 421, 468.
 — see Kullgren.
 DYCK, A. W. T., and McKIBBIN, R. R., Formation of humus, 554, 563.
 DZIENGEL, K., see Hess.
- E
- EASTHAM, A. M., FISHER, H. E., KULKA, M., and HIBBERT, H., Syntheses of wood ethanolysis products, 315.
 EASTWOOD, P. R., see Bray.
 EDDY, C. R., see Speiser.
 EDER, K. W., see Staudinger.
 EDLUND, T., see Klason.
 EDWARDS, V. P., see Wells.
 EHRLICH, F., Chemistry of pectin, 153.
 EICHLER, O., Determination of lignin, 328.
 EIDEM, I., see Hägglund.
 EINSTEIN, A., Viscosity of solutions, 67.
 EISENHUT, O., Oxidative degradation of cellulose, 82.
 EISENHUT, O., and KUHN, E., Structure of artificial cellulose fibers, 69.
 EISENRING, F., see Heuser.
 EKENSTAM, A. AF, Kinetics of cellulose breakdown, 80, 97, 169, 171.
 — Sulfolysis of cellulose, 87, 170.
 — see Schwalbe.
 — see Staudinger.
 EKMAN, C. D., Sulfite pulping, 414.
 EKSTRÖM, G., Wood saccharification by concentrated sulfuric acid, 401.
 — Ethylalcohol from sulfite waste liquor, 458, 472.
 EKWALL, A., see Hägglund.
 ELLER, W., Phenol humic acids, 554, 563.
 ELLER, W., and KOCH, K., Phenol humic acids, 554, 563.
 ELLER, W., and SCHOPPACH, A., Phenol humic acids, 554, 563.
 ELLIS, J. W., and BATH, F., Hydrogen bonds in cellulose, 54, 165.
 ELLMER, L., see Adler.
 ELLRAM, W., Color reactions of wood, 187, 369.
 ELSNER, B., see Fuchs.
 ELSNER, H., see Schlubach.
 EMDE, H., and SCHARTNER, H., Tsugalactone, tsugaresinol, 322, 385.
 EMMETT, P. H., Adsorption of gases by fibers, 55, 165.
 ENDER, W., and UEBEL, O., Determination of lignin, 328.
 ENEBO, L., Pectin fermentation, 110, 172.
 — Products from thermophilic cellulose fermentation, 111, 113.
 ENEBO, L., JOHNSSON, E., and LUNDIN, H., Fermentation of concentrated sulfite waste liquor, 461.
 ENEROTH, O., Relation between heartwood content and age of the tree, 15, 27.
 — Specific gravity of wood, 35, 36.
 ENG, H., ÖSTERLÖF, J., and SILLÉN, L. G., Sulfate ions in sulfite waste liquor, 427, 468.
 ENGEL, O., and WEDEKIND, E., Pulping with dioxane, 244.
 ENGEL, O., see Wedekind.
 ENGEL, W., see Hess.
 ENGELSTAD, A., see Cross.
 ENGLER, K., see Freudenberg.
 ENKVIST, T., Thioglignin, 213, 486.
 — Equivalent weight of alkali lignin, 486.
 — Molecular weight of thioglignin and alkali lignin, 484.
 — Phytosterols from tall oil, 492.
 ENKVIST, T., and HÄGGLUND, E., Reaction of different lignin preparations with sodium hydrosulfide, 213.
 — Thioglignin, 483.
 ENKVIST, T., and MOILANEN, M., Model reactions for sulfate cooking, 484, 485, 495.
 ENKVIST, T., MOILANEN, M., and ALFREDSSON, B., Formation of thioglignin, 213, 372.
 — Migration of lignin in wood during hydrogen sulfide cook, 484, 495.
 — Water soluble lignin in black liquor, 487, 495.
 ENOKSSON, B., Osmotic balance, 70.
 ERASMUS, P., see Bergius.
 ERBRING, H., and PETER, H., Shape of pine glycol and glycerol lignin molecules, 296.
 ERDMANN, E., Distillation of pine lignin, 267.
 — Coal formation from cellulose, 553.
 ERDMANN, E., and SCHAEFER, C., Dry distillation of cellulose, 108.
 — Formation of tar during wood distillation, 534, 539.
 ERDMANN, J., Linkage between different wood constituents, 38, 297.

- ERDTMAN, H., Arabinose from pine heart-wood, 143.
- Sulfonation of lignin in the presence of phenols, 197, 205.
- Dehydrodiisoeugenol, 199, 313.
- Groups A and B in lignin, 207.
- Precipitation of lignosulfonic acid by organic bases, 221, 222, 285, 434, 469.
- Methylation of lignosulfonic acid, 223, 373.
- Bromination of lignin, 281.
- Precursors in the biosynthesis of lignin, 308, 310, 312.
- Oxygen-containing rings in lignin, 313.
- Sulfite liquor lactone (conidendrin), 322.
- Dehydrogenation and biosynthesis of lignin, 323.
- Lignans, 339, 343, 388.
- Pinoresinol, 341, 388.
- Gmelinol, 341, 388.
- Conidendrin in conifers, 342.
- Pino-sylvin and its methyl ethers, 343, 344, 444.
- Flavones and flavanones from pine heart wood, 346.
- Phenolic constituents of pine heart wood, 444, 446, 447.
- Sulfite pulping of spruce branch wood, 447.
- Sulfite pulping of spruce pole thicket wood, 448, 470.
- Polymerization of phenols and quinones, 554.
- Reduction of humic acids, 556.
- ERDTMAN, H., ERICSON, P., and HÄGG-LUND, E., Fractionation of sulfite waste liquors, 222, 434, 469.
- ERDTMAN, H., and GRIPENBERG, J., Thujaplicins, 344.
- ERDTMAN, H., and LEOPOLD, B., Lignin sulfonation models, 203, 234, 314, 323, 384.
- ERDTMAN, H., and LINDBERG, B., Demethylation of conidendrin, 342, 388.
- ERDTMAN, H., LINDGREN, B. O., and PETERSSON, T., Decrease of hydroxyl groups on sulfonation of lignin, 205, 315.
- ERDTMAN, H., and PETERSSON, T., Sulfonation of ethoxylated lignosulfonic acids, 210, 371.
- ERDTMAN, H., and RENNERFELT, E., Occurrence of pino-sylvin and pino-sylvin monomethylether in *Pinus* species, 344, 388.
- ERDTMAN, H., see Anderson.
- see Aulin-Erdtman.
- see Hägglund.
- ERICSON, P., see Erdtman.
- ERIKSSON, T., see Hägglund.
- ERNSBERGER, F. M., and FRANCE, W. G., Molecular weight of lignosulfonic acid, 224.
- ESCHER, E., see Karrer.
- ESCOURROU, R., and CARPENTIER, P., Hydrogen ion concentration in cooking acids, 422.
- ETTI, C., Color reactions of wood, 185, 369.
- EULER, H. v., see Adler.
- EVANS, T. F., see Ritter.
- EVANS, T. H., see West.
- EVANS, W. L., see Gehman.
- EVERT, J. N., see McGovern.
- EWEN, M. F., and TOMLINSON, G. H., Wood saccharification with sulfurous and dilute sulfuric acids, 392.

F

- FABRICIUS, L., Fat and starch in parenchyma cells, 7, 27.
- FÄRBER, E., see Bergius.
- see Hägglund.
- FÄGERLIND, O., see Bergström.
- see Klason.
- FÄHRÆUS, G., Cellulose decomposing cytophaga, 112, 114.
- FAITH, W. L., Wood saccharification, 396, 412.
- FALCK, R., Formation of humus, 554, 563.
- FALK, H., Analysis of sulfate turpentine, 491.
- FALKENHAUSEN, F. v., see Kalb.
- FARR, W. K., Constitution of the cell wall, 40, 361.
- FAUST, O., State of cellulose in solutions, 64.
- FEHLING, H., Action of sulfuric acid on cellulose, 86.
- FEHRM, B., see Hägglund.
- FELDTMANN, G. A., Nitric acid pulping, 504, 505.
- see Schwalbe.
- FELLENBERG, T. v., Saponification of pectin, 154.
- FENNEL, F. L., see Kingsbury.
- FERNANDEZ, O., and ROGUEIRO, B., Degradation of lignin by molds 304, 559.
- Vanillin formation in wood decay 560, 564.
- FEUERSTEIN, K., see Pauly.
- FICHTNER, F., see Lieser.
- FIEDLER, F., see Noll.
- FIERZ-DAVID, H. E., and HANNIG, M., Pressure hydrogenation of lignin, wood, and cellulose, 268, 274, 379.
- FIESER, L., and CAMPBELL, W. P., Abietic and levopimaric acids, 338, 388.

- FIGUIER, L., see Poumarède.
- FILIMONOWA, G., see Komarow.
- FINGERLING, G., and HONCAMP, F., Nutritive value of *Torula* yeast, 399, 412.
- FINK, F., see Jayme.
- FINK, H., and LECHNER, R., Production of yeast from wood sugar, 399.
- Production of yeast from sulfite waste liquor, 463.
- FINK, H., LECHNER, R., and HEINISCH, E., Production of yeast from wood sugar, 399.
- FISCHER, F., Lignin theory of coal formation, 554.
- FISCHER, F., and NIGGEMAN, H., Distillation of cellulose with alkali, 109.
- FISCHER, F., and SCHNEIDER, W., Thermal decomposition of cellulose, 109.
- Pressure heating of cellulose with benzene, 109.
- FISCHER, F., and SCHRADER, H., Decomposition of cellulose by alkali, 103.
- Low temperature tar from cellulose, 109, 172.
- Dry distillation of hydrochloric acid lignin, 268.
- Wood decay, 554, 563.
- FISCHER, F., SCHRADER, H., and FRIEDRICH, A., Wood decay, 554, 557, 563.
- FISCHER, F., SCHRADER, H., and TREIBS, W., Pressure oxidation of lignin, 270, 380.
- Pressure oxidation of cellulose and lignin, 543.
- FISCHER, F., and TROPSCH, H., Dry distillation of cellulose, wood, and lignin, 268.
- Caustic fusion of hydrochloric acid lignin, 269, 379.
- FISHER, E., and BOWER, R. S., Dissolution of lignin with ethanolamines, 254.
- FISHER, G. D., KYAME, L., and BICKFORD, W. G., Norcondendrin, 342, 388.
- FISHER, H. E., and HIBBERT, H., Synthesis of β -hydroxyconiferyl alcohol, 315.
- FISHER, H. E., KULKA, M., and HIBBERT, H., Synthesis and reactions of β -hydroxyconiferyl alcohol methylether, 316.
- FISHER, H. E., see Eastham.
- FLASCHNER, L., and KAST, W., Amorphous and crystalline areas in copper silk, 59.
- FLECHSIG, E., Wood saccharification with sulfuric acid, 400.
- FLECK, E., and PALKIN, S., Dehydro-, dihydro- and tetrahydroabietic acids, 338, 388.
- FLECK, L. C., see Hawley.
- see Ritter.
- FLEURY, P., and POIROTS, G., Color stability of aniline and orcine furfural compounds, 144, 177.
- FLICKINGER, E., see Freudenberg.
- FOERSTER, F., Stability of bisulfite solutions, 424.
- FORDYCE, C. R., see Malm.
- FORMAN, L. V., Sulfite pulping of hardwoods, 490.
- FORMAN, L. V., and NIEMEYER, D. D., Tannin content of different plants, 345.
- Sulfate pulping of hardwoods, 490.
- FORNI, P. A., Color of pulp and lignin content, 506, 528.
- FORSAITH, C. C., Physical properties of wood, 36.
- Lignin content of medullary rays, 306, 384.
- FOTH, G., Wood saccharification with dilute acids, 395.
- FOTIEV, S. A., Chlorine consumed by substitution and oxidation in bleaching, 508, 528.
- Chlorine consumed by substitution in hypochlorite bleaching, 519, 528.
- FOWLER, W. F., see Taylor.
- FOWLER, W. F., JR., see McGee.
- see Unruh.
- FRAHM, H., Reversion of sugar solutions, 99.
- see Hess.
- FRANCE, W. G., see Ernsberger.
- FRANCHIMONT, A. P. N., Cellobiose acetate, 42.
- FRANCK, C., Steam treatment of wood, 550.
- FRANK, A., Treatment of sulfite waste liquor with lime, 228.
- FRANK, R. L., see Adkins.
- FRANKEVICS, J., and BEARSE, N. J., Hypochlorite bleaching and α -cellulose content, 526, 530.
- FRANKL, H., Constituents of wood tar, 534, 539.
- FRANZ, A., Pulping with chlorine, 502, 505.
- FRANZ, E., and HENNING, H. J., Strength of cellulose fibers, 117.
- FRANZ, E., and SCHIEBOLD, E., Electron microscopy of bacterial cellulose films, 58, 165.
- FRANZ, E., SCHIEBOLD, E., and WEYGAND, C., Electron microscopy of bacterial cellulose films, 58, 165.
- FRANZ, E., see Dolmetsch.
- FRAZIER, W. C., see Peterson.

- FREDENHAGEN, K., and CADENBACH, G., Digestion of wood and cellulose with hydrofluoric acid, 101, 328, 410.
- FREDENHAGEN, K., and HELFERICH, B., Digestion of wood and cellulose with hydrofluoric acid, 410, 413.
- FREEMAN, R. D., and PETERSEN, F. C., Chemical analysis of some woods, 352, 390.
- FRÉMY, E., and TERREIL, A., Wood constituents, 39.
- Determination of cellulose, 125.
- FREUDENBERG, K., Acetolysis of cellulose, 42.
- Cellobiose, 42.
- Kinetics of cellulose breakdown, 97, 171.
- Phloroglucinol reaction of wood, 187.
- Treatment of lignin with lead tetraacetate, 199.
- Sulfonation of lignin, 199.
- Ether oxygen in lignin, 214, 372.
- Nitrobenzene oxidation of lignin and lignosulfonic acid, 231, 374.
- Phenol lignin, 247, 377.
- Oxidation of methyl lignin, 272.
- Structure of lignin, 274, 308.
- Formation of formaldehyde from lignin, 290.
- Formation of formaldehyde from lignin model substances, 291.
- Elementary composition of lignin, 284, 381.
- Aliphatic hydroxyl groups in lignin, 286, 381.
- Distribution of the oxygen functions of lignin, 286, 313, 381.
- Bromination of lignin, 289, 370.
- Wood morphology, 298, 383.
- Separation of wood polyoses and cellulose from lignin, 305.
- Isohemipinic acid from lignin, 310, 311.
- Optical inactivity of lignin, 323, 385.
- Formation of a lignin-like substance by the action of phenol oxidase on coniferyl alcohol, 324.
- Determination of acetyl groups in wood, 349.
- FREUDENBERG, K., and ACKER, L., Glycol chlorohydrin as lignin solvent, 243.
- Formation of formaldehyde from lignin, 291.
- FREUDENBERG, K., and ADAM, K., Low temperature distillation of lignin, 268.
- FREUDENBERG, K., ANDERSEN, C., and GO, Y., Oligosaccharides from cellulose, 44, 163.
- FREUDENBERG, K., BELZ, W., and NIEMANN, C., Chlorination (bromination) of lignin, 125, 174, 507, 512, 528.
- Elementary composition of lignin, 199, 370.
- Bromination of lignin, 272.
- Methoxyl content of lignin, 284, 381.
- Double bonds in lignin, 289, 370.
- FREUDENBERG, K., and BLOMQUIST, G., β -Glucosidic structure of cellulose, 45, 163.
- Kinetics of the hydrolysis of cellulose, 80, 87, 88, 169, 170.
- Sulfolysis of cellulose, 87, 170.
- FREUDENBERG, K., and BOPPEL, H., End groups in cellulose, 47, 164.
- Viscosity of methyl cellulose, 49, 164.
- α -Glucosidic structure of starch, 54, 165.
- FREUDENBERG, K., and BRAUN, E., End-group determination in cellulose, 47, 164.
- FREUDENBERG, K., BRUCH, E., and RAU, H., Structure of the cellulose molecule, 50, 164.
- FREUDENBERG, K., and DIETRICH, G., Oxygen balance of cuproxam lignin, 286.
- FREUDENBERG, K., and DÜRR, W., Effect of nitric acid on hydrochloric acid lignin, 270.
- Wood fiber model, 452.
- Treatment of methyl lignin with N_2O_4 , 270, 271.
- Oxidation of lignin with ozone, 271.
- FREUDENBERG, K., ENGLER, K., FLICKINGER, E., SOBEK, A., and KLINK, F., Sulfite cooking of methylated wood, 212, 279, 372, 381.
- Degradation of lignin, 279, 381.
- Formation of formaldehyde from lignin, 290, 382.
- FREUDENBERG, K., and FRIEDRICH, K., Oligosaccharides from cellulose, 44, 163.
- FREUDENBERG, K., FRIEDRICH, K., and BUMANN, I., Cellotetraose, 43, 163.
- FREUDENBERG, K., and HARDER, M., Formation of formaldehyde from hydrochloric acid lignin, 290.
- FREUDENBERG, K., HARDNER, M., and MARKERT, L., Caustic fusion of hydrochloric acid lignin, 269, 379.
- FREUDENBERG, K., and HEIMBERGER, W., Action of phenol oxidase on coniferyl alcohol, 324.
- FREUDENBERG, K., and HESS, H., Phloroglucinol reaction of wood, 187, 369.
- Cuproxam lignin, 276, 380.
- Phenolic hydroxyl groups in lignin, 286, 381.

- FREUDENBERG, K., JANSON, A., KNOPF, E., and HAAG, A., Extraction of lignin with alcohol-benzene mixtures, 194, 370.
- Formic acid lignin, 252, 306, 377.
 - Caustic fusion of lignin, 278, 310, 380.
- FREUDENBERG, K., and KELLER, R., Action of SO_3 -pyridin on spruce wood, 302, 384.
- FREUDENBERG, K., and KLINK, F., Isohemipinic acid and veratric acid, 310, 384.
- FREUDENBERG, K., KLINK, F., FLICKINGER, E., and SOBEK, A., Formation of formaldehyde from lignin, 291, 382.
- FREUDENBERG, K., and KUHN, W., Sulfolysis of cellulose, 87, 170.
- FREUDENBERG, K., KUHN, W., DÜRR, W., BOLZ, F., and STEINBRUNN, G., Sulfolysis of cellulose, 87, 170.
- FREUDENBERG, K., and LAUTSCH, W., Nitrobenzene oxidation of lignin and lignosulfonic acid, 280.
- FREUDENBERG, K., LAUTSCH, W., and ENGLER, K., Oxidation of spruce wood and lignin with alkali and nitrobenzene, 214, 231, 280, 372.
- FREUDENBERG, K., LAUTSCH, W., and PIAZOLO, G., Sulfite digestion of spruce wood at 70°C, 203, 225.
- Digestion of wood with potassium-liquid ammonia, 278, 302, 380.
- FREUDENBERG, K., LAUTSCH, W., PIAZOLO, G., and SCHEFFER, A., Pressure hydrogenation of lignin, 275, 380.
- FREUDENBERG, K., MEISTER, M., and FLICKINGER, E., Sulfonation of lignin, 199, 371, 535, 539.
- Sulfonation of oxidation product from methylated dehydro-diisoeugenol, 199, 310, 371.
- FREUDENBERG, K., MOLTER, H., and DIETRICH, G., Isolation of xylose and arabinose, 138.
- FREUDENBERG, K., and MÜLLER, W. F., Iodination of lignin, 281, 381.
- FREUDENBERG, K., and NAGAI, W., Oligosaccharides from cellulose, 44, 163.
- FREUDENBERG, K., and PLANKENHORN, E., Tetramethylglucose from cellulose, 47.
- Viscosity of methyl celluloses, 49, 164.
 - Acetic acid lignin, 248, 249.
 - Treatment of cuproxam lignin with acetic acid-magnesium chloride, 284.
 - Formation of formaldehyde from lignin, 291.
 - Phenolic hydroxyl groups in lignin, 286, 381.
 - Breakdown and condensation of lignin, 319, 385.
- FREUDENBERG, K., PLANKENHORN, E., and BOPPEL, H., End groups in cellulose, 47, 164.
- FREUDENBERG, K., and PLOETZ, T., Determination of lignin, 264, 325.
- FREUDENBERG, K., and RICHTZENHAIN, H., Constitution of dehydro-diisoeugenol, 313.
- Action of phenol oxidase on low-molecular substances related to lignin, 323.
- FREUDENBERG, K., RICHTZENHAIN, H., FLICKINGER, E., and ENGLER, K., Condensation of low-molecular lignin models by acids, 265.
- FREUDENBERG, K., and SOFF, K., Kinetics of cellulose breakdown, 97, 171.
- FREUDENBERG, K., and SOHNS, F., Phenol lignin, 247, 377.
- Formation of formaldehyde from hardwood lignin, 278, 380.
 - Iodination of lignin, 281, 381.
- FREUDENBERG, K., SOHNS, F., DÜRR, W., and NIEMANN, C., Action of mercuric acetate on lignin, 277, 380.
- Phenolic hydroxyl groups in lignin, 286, 381.
 - Treatment of cuproxam lignin with lead tetraacetate, 289, 380.
 - Refractive index of lignin, 295, 382.
 - Wood morphology, 298, 383.
- FREUDENBERG, K., SOHNS, F., and JANSON, A., Precipitation of lignosulfonic acids with quinoline, 220, 373.
- Solubility of isolated lignin in dioxane, 244.
 - Caustic fusion of hydrochloric acid lignin, 269, 379.
 - Cuproxam lignin, 276, 311, 380.
 - Hydroxyl groups in lignin, 285, 381.
- FREUDENBERG, K., and WALCH, H., Phenolic hydroxyl groups in lignin, 204, 286, 381.
- FREUDENBERG, K., ZOCHER, H., and DÜRR, W., Cuproxam lignin, 276.
- Refractive index of lignin, 295, 382.
 - Wood morphology, 298, 383.
- FREUDENBERG, K., see Stumpf.
- FREY-WYSSLING, A., Cross-linking of proteins, 48.
- Dimensions of intermicellar spaces in fibers, 55.
 - Cellulose fibrils, 58, 165.
 - Existence of lignin, 182.
- FREY-WYSSLING, A., and MÜHLETHALER, K., Electron microscopy of bacteria cellulose films, 58, 166.
- FREY-WYSSLING, A., and WÄLCHI, O., Intermicellar spaces in cellulose, 55, 165.
- FRIEBERG, A. G., see Briggs.

- FRIEDMAN, L., and McCULLY, C. R., Digestion of wood with benzyl alcohol, 241, 244, 376.
- FRIEDRICH, A., Acetic acid lignin, 248.
— Pressure oxidation of lignin, 270, 380.
- FRIEDRICH, A., and BRÜDA, B., Alcohol lignin, 237, 375.
- FRIEDRICH, A., and DIWALD, J., Alcohol lignin, 237.
- FRIEDRICH, A., see Fischer.
- FRIEDRICH, K., see Freudenberg.
- FRIES, K., and BRANDES, E., Formation of stilbenes, 235, 375.
- FRIES, K. W., Semichemical pulp, 501, 505.
- FRIESE, H., Acetolysis of wood meal, 299.
- FRIESE, H., and FÜRST, H., Nitration of wood meal, 299, 383.
- FRIESE, H., HÖGN, V., and WILLE, H., Lignosulfonic acid-carbohydrate compound, 301, 384.
- FRIESE, H., and LÜDECKE, W., Nitration of wood meal, 270, 299, 383.
- FRIESE, H., and STOECK, G., Lignosulfonic acid-carbohydrate compound, 301, 384.
- FRIESE, H., see Hess.
- FRILETTE, V. J., see Badgley.
— see Brenner.
— see Mark.
- FROEHLKE, A. W., see Sherrard.
- FROMBERG, P. F. K., Incrustation theory, 297.
- FROMHERZ, K., Wood gum, 120.
— Galactan in hardwoods, 152, 178.
- FUCHS, W., Color reactions of wood, 185.
— Thermal decomposition of different lignin preparations, 268.
— Biosynthesis of lignin, 320.
— Indirect determination of lignin, 332.
- FUCHS, W., and BETTELHEIM, L., Phenol lignin, 246.
- FUCHS, W., ELSNER, B., and STIX, W., Sulfonation of lignin, 199.
- FUCHS, W., and HONSIG, E., "Incrusting substance," 180, 368.
- FUCHS, W., and HORN, O., Oxidation of lignin with ozone, 272.
- FUCHS, W., see Hönig.
— see Pringsheim.
- FÜRST, H., see Friese.
- FULMER, E. I., see Veldhuis.
- G
- GABRIEL, H., see Rassow.
- GABRIELSON, C. O., Tall oil, 492.
- GADD, G. O., Effect of SO_2 on fermentation, 461, 472.
- GAMER, C. H., see Othmer.
- GARDNER, J. A. F., and HIBBERT, H., Ethanolysis of β -hydroxyconiferyl-alcohol methylether, 316, 384.
- GARDNER, J. A. F., see Brawn.
- GARRE, W., see Wedekind.
- GAUGER, W. H., see Sherrard.
- GAULIS, M., see Pictet.
- GAY-LUSSAC, J. L., and THENARD, L. J., Elementary composition of wood, 181.
- GEAKE, A., see Birtwell.
- GEHMAN, H., KREIDER, L. C., and EVANS, W. L., Alkali sensitivity of enol-glucosides, 85, 170.
- GEIGER, E., Determination of groups characteristic for oxycellulose, 85.
- GENTZEN, R., and ROTH, L., Effect of oxidants on wood saccharification, 394.
- GEORGES, L. W., see Wolfrom.
- GERNGROSS, O., HERMANN, K., and ABITZ, A., Fringe micelles, 57.
- GIBBS, R. D., Drying velocity of wood, 34.
— Glycol lignin, 243, 376.
— see Creighton.
- GIBSON, W. R., Sodium metaphosphate in bleaching, 518, 529.
- GIDDENS, J. E., see Reeves.
- GIERISCH, W., Determination of pentosans, 120, 143, 174, 177.
— Condensation of aldehydes with barbituric acid, 188, 369.
— see Waentig.
- GIERTZ, H. W., Color of pulp and lignin content, 506, 528.
— Substitution and oxidation in chlorination of sulfite pulps, 509, 528.
— Residual lignin in semibleached pulps, 510, 515, 528.
— Influence of pH on chlorination, 512, 528.
— Chlorine demand for delignification, 514, 528.
— Chlorination and morphological structure of pulp, 514, 528.
— Chlorination of pulp with gaseous chlorine, 514, 528.
— Influence of sulfite cooking conditions on bleachability, 517, 528.
— Alkaline extraction in bleaching, 517, 528.
— Chlorine dioxide bleaching, 522, 529.
— Formation of chlorine dioxide from chlorite, 522, 529.
— Reaction of chlorite with phenols, cresols, and lignin compounds, 523.
— Chlorite bleaching, 523, 529.
— Reaction between formaldehyde and chlorite, 524.
— Action of chlorite ion in bleaching, 524.
— Attack of chlorine on cellulose, 525, 528.

- Bleaching of kraft pulps to high brightness with chlorine dioxide, 526, 528.
- Chlorine dioxide bleaching and color resistance, 526, 530.
- Yellowing of pulp, 527, 530.
- see Hägglund.
- GILLER, O., Formation of carbon dioxide during sulfite cooking, 457.
- GIORDANI, M., Wood saccharification with concentrated sulfuric acid, 401.
- GIRARD, A., Hydrocellulose, 78, 169.
- GLADDING, E. K., and PURVES, C. B., Determination of groups characteristic for oxycellulose, 85, 170.
- GLADDING, E. K., see Heidt.
- GLADING, R. E., Absorption spectrum of lignin, 293, 318.
- Ultraviolet absorption of flavanones, 293.
- GLITSCHER, E. A., see Lieser.
- Go, Y., see Freudenberg.
- GODARD, H. P., MCCARTHY, J. L., and HIBBERT, H., Pressure hydrogenation of maple and spruce wood, 245.
- GODDARD, J. G., see Bond.
- GODET, C., see Schulze.
- GÖTHNER, I., Tall oil, 491, 496.
- GÖTZE, K., Aging of alkali cellulose, 82, 169.
- GOGARTEN, R., Effect of repeated use of acid-sugar solutions in wood saccharification, 397, 412.
- GOLDFINGER, G., Kinetics of sulfite pulping, 421.
- GOLDFINGER, G., MARK, H., and SIGGIA, S., Periodate oxidation and crystallinity of cellulose, 60, 85.
- GOLDINA, S. M., see Koslow.
- GOLDSCHMID, O., see Lovell.
- GOLDSCHMIDT, T., A.-G., and HÄGGLUND, E., Rheinau process, 404, 413.
- GOLOVA, O. R., and IVANOV, V. I., Degree of polymerization of cellulose, 124, 174.
- GOODWIN, W., see Maquenne.
- GORDON, C. V., Corrosion of wood, 552.
- GORTNER, R. A., see Aronovsky.
- see Pervier.
- GORTON, J., see Sandqvist.
- GOSS, M. J., see Phillips.
- GOTTLIEB, E., Elementary composition of wood, 37.
- GRABON, R. H., see Wells.
- GRAFE, V., Hadromal in wood, 183.
- Color reactions of wood, 183.
- Color reaction of wood with hydrochloric acid, 191, 368.
- Vanillin from sulfite waste liquor, 229.
- Linkage between lignin and carbohydrates, 297.
- GRAHAM, J. A., Pulping of pine heartwood, 447.
- GRALÉN, N., Molecular weight of cellulose by sedimentation velocity and diffusion methods, 70, 73, 168.
- Polydispersity of cellulose, 124.
- Molecular weight of alkali lignin, 257, 378.
- Molecular weight of thioglycolic acid lignin, 296.
- Linkage between lignin and carbohydrates, 301.
- GRALÉN, N., and RÂNBY, B., Molecular weight of celluloses, 70, 74, 168.
- GRALÉN, N., and SAMUELSON, O., Molecular weight of celluloses, 70, 168.
- GRALÉN, N., and SVEDBERG, T., Molecular weight of celluloses, 70, 168.
- GRALÉN, N., see Holmberg.
- GRASSMANN, W., STADLER, R., and BENDER, R., Cellulose breakdown by molds, 47, 163.
- GRASSMANN, W., ZECHMEISTER, L., TOTH, G., and STADLER, R., Cellulose breakdown by molds, 47, 163.
- GRAUMANN, E., see Schmidt.
- GRAY, K. R., BRAUNS, F. E., and HIBBERT, H., Treatment of glycol lignin with lead tetraacetate, 289, 382.
- Glycol lignin, 243, 376.
- GRAY, K. R., BRAUNS, F. E., KING, E. G., and HIBBERT, H., Glycol lignin, 243, 376.
- GRAY, K. R., see Hibbert.
- GREEN, H. U. S., Chlorine alkali pulping, 502, 505.
- GREEN, H. U. S., and YORSTON, F. H., Effect of chipping on pulp strength, 450.
- GREEN, J. W., see Heuser.
- GRIESS, W., see Spandau.
- GRIGORESCU, D., see Hess.
- GRIMES, W. S., see Brauns.
- GRIMM, H., see Schwalbe.
- GRIPENBERG, J., Thujaaplicins, 344.
- see Anderson.
- see Erdtman.
- GRÖGAARD, L., Chipping of wood and pulp strength, 451, 472.
- GRONDAL, B., and BERGER, H. W., Fermentation of wood sugar, 399, 412.
- GROSS, H., see Signer.
- GROTH, B., Hydrogen sulfide in sulfite waste liquor, 426.
- GRÜSS, J., Color reactions of wood, 193, 370.
- Alcohol lignin, 237.
- GUILLEMONAT, A., and TRAYNARD, P., Extraction of lignin with alcohol-benzene, 195.
- GUNDERMANN, J., see Hess.

- GUNKEL, L., see Heuser.
 GUSTAFSSON, C., see Sundman.
 GUSTAVSON, K. H., Sulfite waste liquor as tanning agent, 465, 473.
 GUSTAVSON, K. H., and LARSSON, A., Mechanism of tannage by lignosulfonic acids, 465, 473.
 GUSTAVSON, K. H., and TOMLINSON, J., Lignosulfonic acids as tanning agents, 465, 473.
 GUSTAVSSON, S. see Bergek.
 — see Bäckström.

H

- HAAG, A., see Freudenberg.
 HAAR, A. W. VAN DER, Monosaccharides and alduronic acids, 131, 149, 175, 178.
 HAARMANN, W., see Tiemann.
 HAAS, R. H., see Assaf.
 HABRLE, I. A., see Nickerson.
 HACHIYAMA, Y., and SAEGUSA, H., Alcohol lignin, 240.
 HACHIYAMA, Y., and TAKEMURA, W., Nitrophenol derivatives in waste liquors from nitric acid pulping, 270.
 HACHIYAMA, Y., ZYÔDAI, S., and UMEZU, M., Hydrogenation of hydrochloric acid lignin, 275.
 HÄGGLUND, E., Heartwood formation, 15.
 — Average breadth and length of fibers, 21.
 — Saccharification of "sulfite fodder pulp", 94.
 — Cellulose determination, 127, 129, 175.
 — Cellulose content in spruce wood, 128, 131, 175, 356, 390.
 — Galactose in sulfite waste liquor, 151, 178.
 — Galactose content in Cross-Bevan cellulose, 151, 178.
 — Sugars in sulfite waste liquor, 156, 431, 469.
 — Water-soluble wood polyoses in spruce wood, 158.
 — Polysaccharides of cellulose type, 158, 179.
 — Pentoses in spruce wood, 158, 161, 179.
 — Solubility of lignin in strong acids, 182, 368.
 — Alcohol lignin, 195, 370.
 — Sulfonation of lignin, 199, 371.
 — Sulfidation of wood, 212, 372.
 — Addition of hydrogen chloride to lignin, 214, 372.
 — Dissolution of lignosulfonic acid, 216, 372.
 — Precipitation of lignosulfonic acid with amines, 220, 221, 373.
 — Removal of alkoxyl groups from lignosulfonic acid, 226, 373.
 — Caustic fusion of lignin, 227, 374.
 — Sulfite cooking of alcohol lignin, 240, 249, 375.
 — Mechanism of sulfite pulping, 242.
 — Action of highly concentrated hydrochloric acid on wood, 264, 266, 379.
 — Sulfonation of hydrochloric acid lignin, 266.
 — Pressure heating of lignin in alkaline solution, 269.
 — Caustic fusion of hydrochloric acid lignin, 269, 379.
 — Methoxyl content of wood sugar, 285, 381.
 — Ether oxygen in hydrochloric acid lignin, 287, 381.
 — Double bonds in hydrochloric acid lignin, 289.
 — Determination of lignin, 328, 356, 390.
 — Wood saccharification with dilute acids, 392, 401.
 — Wood saccharification with sulfuric acid, 401, 412.
 — Wood saccharification with concentrated hydrochloric acid, 403, 413.
 — Rhinau process, 404, 413.
 — Pulping with sodium bisulfite, 419, 467.
 — Pulp yield from sulfite cooking, 420, 421, 468.
 — Hydrogen ion concentration of cooking liquors, 422, 468.
 — "Burnt cook," 423, 468.
 — Decomposition of sugars during sulfite cooking, 431, 433, 469.
 — Decomposition of bisulfite solutions in the presence of sugars, 431, 469.
 — Relationship between color of sulfite waste liquor and pulp quality, 434, 469.
 — Pulping with Ca and Mg bisulfites, 438.
 — Pulping of pine heartwood, 444, 470.
 — Relationship between the composition of cooking liquor and the pulp quality, 449.
 — Susceptibility of isolated wood fibers to sulfite cooking acid, 450, 470.
 — Acetic and formic acids in sulfite waste liquor, 456, 471.
 — Formation of methanol during sulfite cooking, 457, 462, 472.
 — Alcohol from sulfite waste liquor, 458.
 — Cultivation of yeast on sulfite waste liquor, 463, 472.
 — Composition of black liquor, 475.
 — Consumption of alkali during alkaline pulping, 476, 494.
 — Velocity of soda pulping, 476, 495.

- Dissolution of lignin and carbohydrates in sulfate pulping, 479, 483, 495.
- Strength of sulfate pulp, 482.
- Hydrogen sulfide lignin, 483.
- Change of sulfidity in sulfate cooking, 480.
- Consumption of alkali in sulfate pulping, 476, 494.
- Pulping time and pulp strength in sulfate pulping, 479, 495.
- Destruction of isolated fibers during sulfate pulping, 490, 496.
- By-products from soda pulping, 491, 496.
- Regeneration of alkali from black liquor, 494, 496.
- Bleaching of sulfate pulp, 510, 530.
- Chlorination in bleaching, 514, 528.
- Decrease in viscosity during chlorination, 525, 528.
- Pressure heating of wood with alkali, 543.
- Sulfite cooking of air-dry and green wood, 549, 552.
- Changes of wood during storage, 549, 552.
- HÄGGLUND, E., and ALVFELDT, O., Vanillin yield from lignosulfonic acids, 230.
- HÄGGLUND, E., AMÉEN, W., BERGEK, T., LINDHOLM, I., and NIHLÉN, H., Sulfite pulping of birch wood, 448.
- HÄGGLUND, E., AMÉEN, W., NILSSON, T., JOHANSSON, D., and JOHNSON, T., Wood saccharification with concentrated sulfuric acid, 401, 412.
- HÄGGLUND, E., and ARNOLD, S., Sulfite pulping after acid treatment of wood, 423, 468.
- HÄGGLUND, E., BÄCKSTRÖM, C. H., KARANOVIĆ, M., RUNQUIST, L., and VINCENT, O., Stability of bisulfite solutions, 427, 468.
- HÄGGLUND, E., and BERGIUS, F., Regeneration of alkali from black liquor, 494.
- HÄGGLUND, E., and BJÖRKMAN, C. B., Solubility of lignin in strong acids, 182, 368.
- Caustic fusion of hydrochloric acid lignin, 269, 379.
- Treatment of hydrochloric acid lignin with hydrogen peroxide, 272.
- Distillation of hydrochloric acid lignin with 12 % hydrochloric acid, 290.
- Linkage of lignin with carbohydrates, 301, 384.
- Determination of lignin, 327, 380.
- Formation of sugars during sulfite cooking, 431, 469.
- HÄGGLUND, E., and BOEDEKER, H., Formation of sugars during sulfite cooking, 430, 468.
- HÄGGLUND, E., and BRATT, L. C., Sulfolysis of cellulose, 100.
- Determination of mannan, 146, 178.
- Yield of vanillin from lignosulfonic acids, 230.
- Formation of formaldehyde from lignin, 290.
- HÄGGLUND, E., and CARLSSON, G. E., Lignosulfonic acid, 199, 371.
- Sulfonation of cuproxam lignin, 277, 380.
- HÄGGLUND, E., and EIDEM, I., Sulfate pulping, 476, 495.
- HÄGGLUND, E., EKWALL, A., and HOSTOMSKY, J., Sulfonation of lignin, 418, 467.
- HÄGGLUND, E., ERDTMAN, H., AULIN-ERDTMAN, G., and LINDGREN, B., Sulfonation of lignin, 197, 370.
- HÄGGLUND, E., FEHRM, B., and WAENERLUND, L., Reddening of sulfite pulps, 455.
- HÄGGLUND, E., and GIERTZ, H. W., Determination of lignin in bleached pulps, 327.
- HÄGGLUND, E., GIERTZ, H. W., and NELSON, B., Bleaching of sulfate pulp, 506, 510, 516, 517, 528.
- Chlorine dioxide bleaching, 524, 528.
- HÄGGLUND, E., and HANSEN, S., Pulping of sap- and heartwood, 444, 470.
- HÄGGLUND, E., and HEDBERG, F., Pulping of resinous woods, 447.
- HÄGGLUND, E., and HEDLUND, R., Effect of sulfidity in sulfate pulping, 477, 495.
- Volatile by-products from sulfate pulping, 491, 496.
- HÄGGLUND, E., and HEDMAN, E. O., Reddening of sulfite pulp, 454, 471.
- HÄGGLUND, E., and HEIWINKEL, H., Vanillin from sulfite waste liquor, 230.
- HÄGGLUND, E., HEIWINKEL, H., and BERGEK, T., Fermentation of sulfite waste liquor, 434, 469.
- HÄGGLUND, E., and HOLMBERG, J., Change of the number of hydroxyl groups in lignin on sulfonation, 200, 371.
- Chlorination and bromination of hydrochloric acid lignin, 289.
- HÄGGLUND, E., HOLMBERG, J., and JOHNSON, T., Pulping of pine heartwood, 444, 470.
- HÄGGLUND, E., and JOHANSSON, A., Acidity of cooking liquors, 422.
- HÄGGLUND, E., and JOHNSON, T., Pentosan content in spring- and summerwood from spruce, 161.

- Heating of wood with amines and phenols, 186.
- Dissociation of solid lignosulfonic acid, 216, 372.
- Separation of α - and β -lignosulfonic acids, 221.
- Phenol lignin, 247, 377.
- Sulfonation of hydrochloric acid lignin, 266, 379.
- Fluorescence of lignosulfonic acid, 266, 379.
- Chemical composition of spring- and summerwood from spruce, 352.
- "Burnt cook," 423, 468.
- Decomposition of bisulfite solutions in the presence of sugars, 431, 469.
- Pulping with sulfurous acid, 437, 469.
- Identification of pine heart- and sapwood by ultraviolet light, 445, 470.
- Fluorescence of sulfite pulp, 455, 471.
- Effect of sulfur in sulfate pulping, 488.
- HÄGGLUND, E., JOHNSON, T., and BUSCH, H., Sulfonation of lignin, 197, 205, 370, 418, 420, 467.
- HÄGGLUND, E., JOHNSON, T., and TRYGG, L. H., Carbonyl groups in lignin, 434, 455.
- Change in color of the cooking liquor during sulfite cooking, 434.
- Fluorescence of sulfite pulp, 455.
- HÄGGLUND, E., JOHNSON, T., and URBAN, H., Decomposition of bisulfite solutions in the presence of sugars, 431, 469.
- HÄGGLUND, E., JULLANDER, A., MANNBRO, N., and WAENERLUND, L., Formation of sulfate during sulfite pulping, 428.
- HÄGGLUND, E., and KLINGSTEDT, F. W., Determination of pentosan, 120, 143, 177.
- Optical rotation of cellulose solutions, 121.
- Cellulose content of spruce wood, 128.
- Determination of mannan, 145, 146, 178.
- Identification of galactan in spruce sulfite pulp, 151.
- Fructan in spruce sulfite pulp, 153, 158, 178.
- Solubility of hydroxymethylfurfural phloroglucide in alcohol, 159.
- Ultraviolet absorption of lignin, 292.
- HÄGGLUND, E., KLINGSTEDT, F. W., ROSENQVIST, T., and URBAN, H., Galacturonic acid in sulfite waste liquor, 154.
- HÄGGLUND, E., KOCH, FR., and LÖFMAN, N., Wood saccharification, 406, 413.
- HÄGGLUND, E., and LARSON, R., Hydrolysis of spruce wood with buffer solutions, 149, 178, 430.
- HÄGGLUND, E., and LARSSON, A., Lignosulfonic acids from aspen, 198, 370.
- HÄGGLUND, E., and LARSSON, S., Sulfite cooking of spruce branch wood, 447.
- HÄGGLUND, E., and LJUNGREN, S., Holocellulose, 136, 176.
- Chemical composition of compression wood, 357.
- HÄGGLUND, E., LJUNGREN, S., NIHLÉN, H., and SANDELIN, O., Pentosan content of pine wood, 160, 180.
- Acetyl and formyl contents of pine wood, 350, 390.
- HÄGGLUND, E., LÖFMAN, N., and FÄRBER, E., Cellulose acetate, 120.
- HÄGGLUND, E., and MENZINSKY, G., Reaction of glycol aldehyde with sulfite, 205.
- HÄGGLUND, E., and NELSON, B., Liquor color and pulp quality, 435.
- HÄGGLUND, E., and NIHLÉN, H., Pulp yield from sulfite cooking, 418, 421, 467.
- Sugar yield in sulfite cooking, 433.
- HÄGGLUND, E., and PROFFE, B., Cellulose content of spruce wood, 129, 175.
- Determination of mannan, 146, 178.
- HÄGGLUND, E., and RINGBOM, A., Addition of bisulfite to double bonds, 197, 370.
- HÄGGLUND, E., and ROSENQVIST, T., Determination of pentosan, 143, 177.
- Vanillic acid from the thermal decomposition of lignin, 268.
- Distillation of hydrochloric acid lignin with 12 % hydrochloric acid, 290.
- HÄGGLUND, E., and SANDELIN, O., Methoxyl content of lignin, 194.
- Methoxyl content of carbohydrates in spruce wood, 285.
- Methoxyl content of spruce wood, 331.
- HÄGGLUND, E., SANDELIN, O., NYMAN, C., ERIKSSON, T., and KOSKULL, H. v., Pentosan content of different spruce woods, 160, 179.
- Acetyl and formyl contents of spruce wood, 350, 390.
- HÄGGLUND, E., SANDELIN, O., NYMAN, C., ERIKSSON, T., KOSKULL, H. v., LJUNGREN, S., and NIHLÉN, H., Wood character and pulp quality, 439, 470.
- HÄGGLUND, E., STOCKMAN, L., and LÖFSTRÖM, P., Sulfite pulping with "mixed liquor", 433.
- HÄGGLUND, E., and SÄVÖ, G., Determination of lignin, 326, 386.
- Dissolution of solid lignosulfonic acid, 216, 372.

- HÄGGLUND, E., and SUNDROOS, B., Methoxyl groups in spruce lignin, 238.
— Acetaldehyde in sulfite alcohol, 462.
- HÄGGLUND, E., TUOMINEN, M., and LINDBLOM, K., Regeneration of alkali from black liquor, 494.
- HÄGGLUND, E., and URBAN, H., Alcohol lignin, 195, 238, 251, 370, 377.
— Treatment of hydrochloric acid lignin with acidified alcohols, 249, 377.
— Methylenedioxy groups in lignin, 290, 291.
— Molecular weight of alcohol lignins, 295, 382.
— Formation of formaldehyde from lignin, 290, 291.
— Molecular weight of amyl lignin, 285.
— Methoxyl content of lignin, 331, 386.
— Decomposition of bisulfite solutions in the presence of sugars, 431, 469.
— Bleaching of sulfate pulp, 510.
- HÄGGLUND, E., and WAENERLUND, L., Formation of sulfate ions in sulfite cooking liquor, 426.
- HÄGGLUND, E., and WALLER, A., Dissolution of solid lignosulfonic acid, 216, 372.
- HÄGGLUND, E., and WEBJÖRN, B., Swelling of holocellulose, 360.
- HÄGGLUND, E., see Enkvist.
— see Erdtman.
— see Goldschmidt.
— see Heiwinkel.
— see Stockman.
- HÄGGLUND, S. E., see Aulin-Erdtman.
- HÄGGROTH, S., see Adler.
- HÄLLSTRÖM, M. AF, Determination of molecular weight, 296, 484.
- HÄGLUND, G., Pulping of pine heartwood according to the Graham method, 447, 470.
- HAGSTRÖM, N. F., see Schwalbe.
- HAHN, E., see Schwabe.
- HAJNY, G. J., see Harris.
— see Leonard.
- HALL, L., see DORÉE.
- HALLER, R., Color reaction of lignin with ferric chloride-ferricyanide, 190, 369.
- HALSE, O., and DEDICHEN, H., Volatile by-products from sulfate pulping, 491, 496.
- HAMBURGER, R., and KAESZ, S., Chlorine dioxide as bleaching agent, 521, 529.
- HAMER, P. L., see Wise.
- HAMPTON, H. A., HAWORTH, W. N., and HIRST, E. L., Structure of xylan, 141.
- HANKE, G., see Jayme.
- HANNAN, M., see Harris.
- HANNIG, M., see Fierz-David.
- HANSEN, L. A., see Stamm.
- HANSEN, S., see Hägglund.
- HANSON, F. E., Thiolignin, 482.
- HANUŠ, J., Determination of vanillin, 229.
- HARDER, M., see Freudenberg.
- HARDERS-STEINHÄUSER, M., see Jayme.
- HARDT-STEMAYR, E. R. V., Cellobiose, 42, 162.
- HARLOW, W. M., Nature and distribution of lignin in wood, 305.
- HARLOW, W. M., and WISE, L. E., Lignin content of medullary rays, 306, 384.
- HARLOW, W. M., see Wise.
- HARMUTH, R., Phenol lignin, 246, 377.
- HARRIS, C. A., and PURVES, C. B., Reaction of cellulose with thallium ethylate, 60.
- HARRIS, C. R., see Wheeler.
- HARRIS, E. E., Sulfuric acid lignin, 263, 264.
— Wood saccharification, 411.
- HARRIS, E. E., and ADKINS, H., Pressure hydrogenation of lignin, 275.
- HARRIS, E. E., and BEGLINGER, E., Alcoholic fermentation of wood hydrolyzates, 399, 412.
- HARRIS, E. E., BEGLINGER, E., HAJNY, G. J., and SHERRARD, E. C., Fermentation of wood hydrolyzates with *Clostridium acetobutylicum*, 399, 412.
- HARRIS, E. E., D'IANI, J., and ADKINS, H., Pressure hydrogenation of lignin, 244, 275, 281, 380.
- HARRIS, E. E., HAJNY, G. J., HANNAN, M., and ROGER, S. C., Alcoholic fermentation of wood hydrolyzates, 399, 412.
- HARRIS, E. E., and LOEDAHLE, L. J., Chlorination of lignin, 289.
- HARRIS, E. E., and MITCHELL, R. L., Determination of lignin, 327, 386.
- HARRIS, E. E., SAEMAN, J. F., and BERGSTROM, C. B., Pressure hydrogenation of alkali lignin, 259.
- HARRIS, E. E., SAEMAN, J. F., and SHERRARD, E. C., Hydrogenation of lignin, 275.
- HARRIS, E. E., SHERRARD, E. C., and MITCHELL, R. L., Sulfuric acid lignin, 263, 378.
— Addition of halogens to lignin, 289, 381.
— Hydroxyl groups in lignin, 299.
- HARRIS, E. E., see Cohen.
— see Saeman.
— see Stamm.
- HARRIS, G. C., and SANDERSON, T. F., Dextro- and iso-dextropimaric acids, 337.
— Neo-abietic acid, 338, 388.

- HARRIS, M., see Martin.
 — see Rutherford.
 — see Sookne.
- HARTIG, R., Nitrogen content of beech wood, 347.
 — Decomposition of wood by *Trametes pini*, 558.
- HASCHE, R. L., By-products from wood saccharification, 400, 412.
- HASNER, L., see Schwabe.
- HASSELSTRÖM, T., Composition of sulfate soap, 335.
 — Tall oil, 492.
- HASSELSTRÖM, T., McPHERSON, J., and HOPKINS, S., Tall oil, 492, 496.
- HATCH, R. S., Sulfite pulping with Na-, NH₄-, and Mg-bisulfites, 438.
- HAUG, A., see Heuser.
- HAUG, K., see Samuelsen.
- HAUSEN, J., Keebra process, 498, 504.
- HAUSER, O., and HERZFELD, H., Hydrocellulose, 78, 169.
- HAUSER, S. J., and BAHLMAN, C., Resistance of wood against chemicals, 551.
- HAWKINS, W. L., see Bell.
 — see Brickman.
 — see Dobland.
 — see Patterson.
 — see West.
- HAWLEY, L. F., Wood distillation, 531, 539.
 — Dry distillation of American hardwoods, 536.
 — By-products from wood carbonization, 537.
 — Plasticity of wood during carbonization, 538, 539.
- HAWLEY, L. F., and AIYAR, S. S., Formation of methane and acetic acid during wood carbonization, 534, 536, 539.
- HAWLEY, L. F., FLECK, L. G., and RICHARDS, C. A., Decomposition of spruce wood by *Polyporus hirsutus*, 558.
- HAWLEY, L. F., and NORMAN, A. G., Definition of hemicelluloses, 135.
- HAWLEY, L. F., and WISE, L. E., Wood carbonization, 533, 539.
 — Composition of wood balsams, 334, 387.
- HAWORTH, R. D., Lignans, 339, 343.
- HAWORTH, R. D., and KELLY, W., Lariciresinol, 341, 388.
- HAWORTH, R. D., and RICHARDSON, T., Matairesinol, 340, 388.
- HAWORTH, R. D., and SHELDRICK, G., Sulfite waste liquor lactone, 322.
- HAWORTH, W. N., Pyranose structure of sugars, 43.
 — Hydrolysis of trimethyl cellulose, 44.
 — 1,4-Linkages in cellulose, 51.
- HAWORTH, W. N., HIRST, E. L., and OLIVER, E., Arabinose in xylan preparations, 138, 176.
 — Structure of xylan, 141, 177.
- HAWORTH, W. N., HIRST, E. L., OWEN, L. N., PEAT, S., and AVERILL, F. J., End group determination in cellulose, 47, 164.
- HAWORTH, W. N., and LEITCH, C. G., Methylation of cellulose, 43.
- HAWORTH, W. N., and MACHEMER, H., End group determination in cellulose, 47, 164.
 — Constitution of cellobiose, 43, 163.
- HAWORTH, W. N., MONTONNA, R. E., and PEAT, S., End group determination in cellulose, 47, 164.
- HAWORTH, W. N., PEAT, S., and WILSON, W. J., Chain length of hydrocelluloses, 81.
- HAWORTH, W. N., and PERCIVAL, E. G. V., Structure of xylan, 141, 177.
- HAWORTH, W. N., see Bywater.
 — see Charlton.
 — see Hampton.
- HEAD, F. S. H., Model experiments on oxycellulose, 85.
- HEARON, W. M., see Lackey.
- HEDBORG, F., Alkaline extraction of sulfate pulp, 517, 518, 528.
 — see Hägglund.
- HEDDLE, R. D., see Brawn.
- HEDÉN, S., and HOLMBERG, B., Mechanism of lignin sulfonation, 202, 371.
- HEDENSTRÖM, A. v., Oxalic acid from cellulose and wood, 540.
- HEDLUND, I., Condensation of low-sulfonated lignosulfonic acid, 423.
- HEDLUND, R., see Hägglund.
- HEDMAN, E. O., see Hägglund.
- HEIDENSTAM, G. v., see Klason.
- HEIDT, L. J., GLADDING, E. K., and PURVES, C. B., Cleavage of glycols, 519.
 — Oxidation potentials of bleaching agents, 525, 529.
- HEIMBERGER, W., see Freudenberg.
- HEINISCH, E., see Fink.
- HEIWINKEL, H., Isolation of mannose from β -lignosulfonic acid, 223, 373.
 — Sulfite cooking of holocellulose, 433, 469.
- HEIWINKEL, H., and HÄGGLUND, E., Chlorination of lignin in bleaching, 507, 528.
 — Estimation of chlorine consumed through oxidation and substitution, 514, 528.
 — Decrease of the viscosity of cellulose during chlorination, 525, 528.
- HEIWINKEL, H., see Hägglund.

- HELPERICH, B., and BÖTTGER, S., Action of hydrogen fluoride on cellulose, 101, 328.
- HELPERICH, B., see Fredenhagen.
- HELGER, R., Color reactions of wood, 187, 369.
- HELLRIEGEL, E., see Hillmer.
- HELLSTRÖM, A., Volatile by-products from sulfate pulping, 491, 496.
- HELLSTRÖM, N., Composition of fusel oil, 462.
- Composition of wood tar, 535.
- HELLWAGE, H., see Hilpert.
- HENGLEIN, F. A., Chemistry of pectins, 154.
- HENGSTENBERG, J., and MARK, H., Dimensions of the cellulose micelle, 92.
- see Staudinger.
- HENNEBERG, W., Determination of cellulose, 126.
- HENNIG, T., Precipitation of lignosulfonic acid with fuchsine, 220.
- HENNING, H. J., see Franz.
- HERITAGE, C. C., CURRAN, C. E., MONSON, W. H., and CHIDESTER, E. H., High-yield acid sulfite pulping, 499, 504.
- HERMANN, F., see Heuser.
- HERMANS, I. I., Shape of cellulose molecules 76.
- see Hermans, P. H.
- HERMANS, P. H., Strength of the primary valence bond in cellulose, 116, 173.
- Grinding of dry cellulose, 57.
- Fringe micelle, 121, 165.
- Density of crystalline cellulose, 61, 166.
- Cellulose hydrate filaments, 65, 167.
- HERMANS, P. H., BOOYS, J. DE, and MAAN, C. H., Stereochemistry of cellulose, 54.
- HERMANS, P. H., HERMANS, I. I., and VERMAAS, D., Specific gravity and crystallinity of cellulose, 59, 166.
- HERMANS, P. H., and LEEUW, A. J. DE, Cellulose hydrate filaments, 65, 167.
- HERMANS, P. H., and PLATZKE, P., Stretching and crystallinity of cellulose, 65, 167.
- HERMANS, P. H., and WEIDINGER, A., Amorphous and crystalline regions in cellulose, 59, 60, 166.
- Increase in crystallinity of cellulose fibers on acid hydrolysis, 62.
- Recrystallization of pulverized cellulose, 62, 118, 173.
- HERRBACH, P., see Staudinger.
- HERRMANN, F., see Heuser.
- HERZFELD, H., see Hauser.
- HERZOG, R. O., Hydrocellulose, 78.
- HERZOG, R. O., and HILLMER, A., Phenol lignin, 246.
- Ultraviolet absorption of lignin preparations, 292.
- HERZOG, R. O., and JANCKE, W., Crystalline structure of cellulose, 50, 164.
- HESS, H., see Freudenberg.
- HESS, K., Skeletal and reserve cellulose, 40, 160, 364, 390.
- Attendant carbohydrates, 40.
- End groups in cellulose, 47, 164.
- Structure of the cellulose molecule, 50.
- Cellulose micelles, 64, 166.
- Mercerization of cellulose, 77, 168.
- Cellulose A, 79, 169.
- Oxycellulose, 81, 169.
- Existence of lignin, 182.
- HESS, K., and AKIM, L., Strength of the cellulose fiber, 79, 169.
- HESS, K., DZIENGEL, K., and MAAS, H., End group determination in cellulose, 45, 163.
- HESS, K., and ENGEL, W., Wax and pectin in cotton fiber, 40.
- HESS, K., and FRIESE, H., Hydrolysis of linters, 100.
- HESS, K., GRIGORESCU, D., STEURER, E., and FRAHM, H., Determination of 2,3,4,6-tetramethylglucose, 47, 164.
- HESS, K., and HEUMANN, K. E., Mechanical degradation of cellulose, 118, 173.
- Action of hydrazine on straw lignin, 186, 254.
- HESS, K. P., JUNG, K. P., and HEUMANN, K. E., Grinding of wood and cellulose in an oscillating beater, 300.
- HESS, K., KIESSIG, H., and GUNDERMANN, J., Grinding of cellulose in an oscillating beater, 58, 86, 118, 165, 170.
- Formation of "elementary fibrils", 58, 165, 366, 390.
- Recrystallization of pulverized cellulose, 62.
- HESS, K., and LÜDTKE, M., Spruce wood- and bamboo xylan, 140.
- Isolation of mannan from wood, 144, 177.
- HESS, K., LÜDTKE, M., and REIN, H., Glucan in beech wood, 150.
- HESS, K., and NEUMANN, F., Determination of 2,3,4,6-tetramethylglucose, 47, 164.
- HESS, K., and RABINOWITSCH, B., Strength of the cellulose fiber, 79, 169.
- HESS, K., and STEURER, E., Relation between end group value and viscosity, 48, 164.

- HESS, K., STRICKER, F., and RUTKOWSKI, R., Reaction product from glucose and hydrogen chloride, 101.
- HESS, K., and TROGUS, C., Swelling of cellulose in sodium hydroxide solution, 77, 168.
- HESS, K., TROGUS, C., AKIM, L., and SAKURADA, A., Size of the cellulose micells, 55, 165.
- Strength of the cellulose fiber, 79, 169.
- HESS, K., and ULMANN, M., Structure of the cellulose molecule, 50, 164.
- Breakdown of cellulose with gaseous hydrogen chloride, 101.
- HESS, K., WERGIN, W., TROGUS, C., and GUNDERMANN, J., Cellulose formation in plant fibers, 40.
- HESS, K., and YÜ-CHARNG HWANG, Action of hydrazine on straw, 254.
- HESS, K., see Schlubach.
- HEUBERGER, A., see Wuhrmann.
- HEUER, W., see Staudinger.
- HEUMANN, K. E., see Hess.
- HEUSER, E., Cross-linking in cellulose, 49.
- Crystalline structure of textile fibers, 50.
- Hydrocellulose, 78, 169.
- Isolation of pentosans, 138, 176.
- Wood saccharification with dilute acids, 394, 411.
- By-products from wood saccharification with dilute acids, 395, 411.
- Wood saccharification, 399, 412.
- Sulfate cooking, 480, 495.
- Dry distillation of black liquor, 493.
- HEUSER, E., and AIYAR, S. S., Cellulose triacetate from wood cellulose, 119.
- HEUSER, E., and BOEDEKER, E., Yield of glucose from wood cellulose, 99.
- Cotton cellulose and wood cellulose, 118.
- HEUSER, E., and CHARBONNIER, H. Y., State of cellulose in solutions, 64.
- HEUSER, E., and DAMMEL, W., Yield of cellobiose from wood cellulose, 119.
- HEUSER, E., and GREEN, J. W., Structure of the cell wall, 40.
- HEUSER, E., and HAUG, A., Cotton cellulose and wood cellulose, 118.
- Xylan in straw cellulose, 161.
- HEUSER, E., and HERRMANN, F., Caustic fusion of cellulose, 103.
- Caustic fusion of wood, 541.
- HEUSER, E., and MERLAU, O., Incrusting material in wood, 136, 181, 176, 368.
- HEUSER, E., NEUENSTEIN, W. V., EISENRING, F., and SCHOTT, W., Hydrocellulose, 78, 169.
- HEUSER, E., ROESCH, H., and GUNKEL, L., Oxidation of lignin with concentrated nitric acid, 270, 380.
- HEUSER, E., and SAMUELSEN, S., Reddening of sulfite pulp, 454.
- HEUSER, E., and SCHERER, A., Formation of acetic acid during wood carbonization, 534, 539.
- HEUSER, E., SHEMA, B. F., SHOCKLEY, W., APPLING, J. W., and MCCOY, J. F., Wood decay by a white rot fungus, 559, 563.
- HEUSER, E., and SIEBER, R., Reactions between amines and wood, 186, 369.
- Reaction of wood with chlorine, 190, 369.
- HEUSER, E., and SKIÖLDEBRAND, C., Dry distillation of hydrochloric acid lignin, 267, 379.
- Determination of lignin, 328.
- HEUSER, E., and WINSVOLD, A., Caustic fusion of lignosulfonic acid in hydrogen atmosphere, 227.
- Caustic fusion of hydrochloric acid lignin, 269.
- Caustic fusion of lignin, 541.
- HEUSER, E., ZEH, L., and ASCHAN, B., By-products from wood saccharification with dilute acids, 395, 411.
- HEWSON, W. B., and HIBBERT, H., Mechanism of alcoholysis, 242, 376.
- HEWSON, W. B., MCCARTHY, J. L., and HIBBERT, H., Mechanism of alcoholysis, 242.
- Breakdown and condensation of lignin, 319, 385.
- HEYMANN, E., and RABINOV, G., Carboxyl groups in cellulose, 46.
- HEYN, A. N., Size of cellulose micelles, 55.
- HIBBERT, H., α -Hydroxy-propionguaiacone, 202.
- Pressure hydrogenation of methanol lignin, 245, 376.
- Mechanism of wood ethanolysis, 308.
- "Lignin units" as respiratory catalysts in plants, 323.
- HIBBERT, H., and BRAUNS, F. E., Alcohol lignin, 195, 370.
- HIBBERT, H., BRAUNS, F. E., and BUCKLAND, I. K., Phenol lignin, 194, 370.
- HIBBERT, H., BUCKLAND, I. K., TOMLINSON, G. H., and LEGER, F., Acetoguaiacone from lignosulfonic acid, 231.
- HIBBERT, H., and KING, E. G., Alcohol lignin, 239.
- HIBBERT, H., KING, E. G., and BRAUNS, F. E., Methylation of lignosulfonic acid, 226, 273.
- HIBBERT, H., and MACKINNEY, H. W., Methyl lignin, 240.
- Structure of lignin, 306.
- HIBBERT, H., and MARION, L., Glycol lignin, 243, 376.

- HIBBERT, H., and MOORE, R. G. D., Hydrogenation of lignin, 290, 382.
- HIBBERT, H., and PERCIVAL, E. G. V., Acid hydrolysis of cellulose, 100.
- HIBBERT, H., and PHILLIPS, J. B., Action of glycerol monochlorohydrin on wood, 243.
- Stearic acid from tall oil, 335, 387.
- HIBBERT, H., and ROWLEY, H. J., Glycol lignin, 243, 376.
- HIBBERT, H., and TOMLINSON, G. H., JR., Vanillin, 466.
- HIBBERT, H., see Barsha.
- see Bell.
- see Brewer.
- see Brickman.
- see Buckland.
- see Cooke.
- see Cramer.
- see Creighton.
- see Dobland.
- see Eastham.
- see Fischer.
- see Gardner.
- see Godard.
- see Gray.
- see Hewson.
- see Hunter.
- see Lovell.
- see Marshall.
- see McCarthy.
- see Patterson.
- see Peniston.
- see Pepper.
- see Plungian.
- see Schwartz.
- see Steeves.
- see Tomlinson.
- see West.
- see White.
- see Wright.
- HIESTER, N. K., MCCARTHY, J. L., and BENSON, H. K., Separation of lignosulfonic acids from sulfite waste liquor by dialysis, 224.
- HILLER, L. A., JR., and PACSU, E., Acid-sensitive hemiacetal linkages in cellulose, 79.
- HILLMER, A., Phenol lignin, 247, 377.
- Ultraviolet absorption of lignin, 292, 382.
- HILLMER, A., and HELLRIEGEL, E., Ultraviolet absorption of lignin, 292, 382.
- HILLMER, A., and PAERSCH, E., Ultraviolet absorption of lignin, 292, 382.
- HILLMER, A., and SCHORNING, P., Ultraviolet absorption of lignin, 292, 382.
- HILLMER, A., see Herzog.
- HILLS, C. H., see Speiser.
- HILPERT, R. S., Existence of lignin, 182.
- Properties of chlorinated and nitrated lignosulfonic acids, 226.
- Determinations of lignin, 326, 328, 386.
- HILPERT, R. S., and HELLWAGE, H., Treatment of beech wood with hydrochloric acid, 181, 265, 368.
- HILPERT, R. S., and LITTMANN, E., Treatment of straw with 72 % sulfuric acid, 181, 265, 368.
- Determination of lignin, 326.
- HILPERT, R. S., and PETERS, O., Acetylation of straw, 181, 368.
- HINTIKKA, S. V., Naphthylamine compounds of lignosulfonic acid, 219, 372.
- HIRST, E. L., JONES, J. K. N., and CAMPBELL, W. G., Arabogalactan, 541.
- see Bywater.
- see Hampton.
- see Haworth.
- see Irvine.
- see Procter.
- HISEY, W. O., and KOON, C. M., The influence of pH on bleaching, 511.
- HOCH, H., and BOHUNEK, H., Wood saccharification with hydrogen fluoride, 411, 412.
- HOCHBERGER, E., see Opfermann.
- HOCHFELDER, L., Caustic fusion of lignin, 227, 374.
- Phenol lignin, 246.
- HOCK, C. W., Cellulose fibrils, 57, 90.
- HODAKOFF, K. V., and KALLISTRATOFF, G. A., Formation of carbon dioxide during sulfite cooking, 457, 471.
- HÖGN, V., see Friese.
- HÖHNEL, F. V., Swelling of cellulose in cuprammonium solution, 360.
- HÖK, W., see Sandqvist.
- HÖLDER, F., see Noll.
- HÖNIG, M., Acetic and formic acids in sulfite waste liquor, 425, 456, 471.
- HÖNIG, M., and FUCHS, W., Caustic fusion of lignosulfonic acid, 227, 228.
- HÖNIG, M., and RUZICKA, W., Vanillin from sulfite waste liquor, 229.
- HÖNIG, M., and SCHUBERT, S., Sulfolysis of cellulose, 86, 170.
- HÖNIG, M., and SPITZER, J., Precipitation of lignosulfonic acids, 219.
- HÖPNER, T., Sugars in sulfite waste liquor, 156.
- HOFE, C. v., see Richtzenhain.
- HOFFER, A., see Kürschner.
- HOFFMEISTER, C., Chemical nature of hadromal, 183.
- HOFFMEISTER, W., Determination of cellulose, 126.
- Color reactions of wood, 187, 369.
- Nitrogen content in the cell wall, 347.

- HOHF, F. P., see Sherrard.
- HOLMBERG, B., Thioglycolic acid lignin, 194, 252, 284.
- Sulfonation of lignin and lignin models, 202, 239, 314.
- "Hypobromite lignin," 215.
- Alcohol lignin, 239.
- Mercapto acid lignins, 253, 284.
- Thiohydracrylic acid lignin 254.
- Alkali lignin, 258.
- Sulfite liquor lactone (conidendrin), 322.
- HOLMBERG, B., and ANDERZÉN, O., Alkali lignin, 255, 378.
- HOLMBERG, B., and GRALÉN, N., Molecular weight of thioglycolic acid lignin, 296.
- HOLMBERG, B., and RUNIUS, S., Alcohol lignin, 195, 238, 239, 284, 370, 375.
- HOLMBERG, B., and SUNESSON, E., L-Borneol from fusel oil, 463.
- HOLMBERG, B., and WINTZELL, T., Caustic fusion of lignin, 227, 374.
- Alkali lignin, 255, 378.
- HOLMBERG, B., see Anderzén.
- see Berg.
- see Hedén.
- HOLMBERG, J., see Hägglund.
- HOLST, G., Preparation of chlorine dioxide, 521, 529.
- Chlorous acid, 522, 529.
- Bleaching of sulfate pulp with chlorine dioxide, 524, 529.
- HOLTAN, E., Yield of cymene from sulfite cooking, 457, 472.
- HOLZER, F. W., Phlobaphenes in kraft pulp, 488, 495.
- Sulfite pulp from fungus attacked Hemlock heartwood, 561.
- HONCAMP, F., see Fingerling.
- HONSIG, E., see Fuchs.
- HOPF, H., see Meyer.
- HOPKINS, S., see Hasselström.
- HOPPE-SEYLER, F., Degradation of cellulose with alkali, 102.
- Linkage between lignin and carbohydrates, 297.
- HORN, O., see Fuchs.
- HOSSFELD, R. L., see Brink.
- see Salvesen.
- HOSTOMSKY, J., see Hägglund.
- HOTTENROTH, V., Determination of lignin, 328.
- see Zellstoff-Fabrik Waldhof.
- HOWARD, G. C., Precipitation of lignosulfonic acid, 465, 466.
- Utilization of lignin, 465, 466, 473.
- HOWELLS, H. P., Determination of pentosan, 143, 177.
- HOWSMON, I. A., Recrystallization during hydrolysis of cellulose, 62.
- HUBER, B., and PRÜTZ, G., Volumes of the different kinds of tissues in wood, 7.
- HUDSON, C. S., see Jackson.
- HÜHN, F., see König.
- HUGHES, E. E., and ACREE, S. F., Determination of pentosan, 143.
- Determination of furfural, 143, 177.
- HUGGINS, M. L., Hydrogen bridges, 53.
- HUKKI, J., see Virtanen.
- HULTZSCH, K., Utilization of terpenes, 492, 497.
- HUMPHREY, C. J., see Kress.
- see Rue.
- HUNTER, M. J., CRAMER, A. B., and HIBBERT, H., Ethanolsysis of maple wood, 241, 376.
- HUNTER, M. J., and HIBBERT, H., Absence of piperonyl groups in lignin, 292, 382.
- HUNTER, M. J., WRIGHT, G. F., and HIBBERT, H., Methylenedioxy groups in lignin, 251.
- Formation of formaldehyde from carbohydrates, 291, 171.
- HUNTER, M. J., see Cramer.
- HUPPMANN, G., see Pummerer.
- HURD, C. B., and CANTOR, G. M., Reversion of sugar solutions, 99.
- HUSEMANN, E., Electron microscopy of cellulose, 57, 165.
- Cross-linkages between cellulosic and non-cellulosic constituents of wood, 141, 177.
- Electron microscopy of degraded cellulose fibers, 90, 171.
- Xylan A and B, 140.
- Viscosimetric investigation of xylans, 142.
- Extraction of mannan from spruce wood, 145.
- HUSEMANN, E., and CARNAP, A., Electron microscopy of degraded cellulose fibers, 90.
- Construction of the cell wall, 366, 390.
- HUSEMANN, E., and CONSBRUCH, K., Criticism of Pacsu's cellulose formula, 90, 171.
- HUSEMANN, E., PLÖTZE, E., and SCHULZ, G. V., Cellulose solutions, 66, 167.
- HUSEMANN, E., and WEBER, O. H., Carboxyl groups in cellulose, 45, 89, 163.
- HUSEMANN, E., see Schulz.
- see Staudinger.
- HUTCHINSON, H. B., and CLAYTON, J., Cellulose decomposing bacteria, 112.

- ILLIG, R., see Lechner.
IRINEU, D., see Schroeter.
IRVINE, J. C., and HIRST, E. L., Methylation of cellulose, 43.
— Hydrolysis of acetylated polysaccharides, 119, 173.
— Furfural from esparto pulp, 161, 180.
IRVINE, J. C., and ROBERTSON, G. I., Cellotriase, 43.
ISAAC, J. F. V., see Cross.
ISELL, H. C., see Jeanes.
ISENBERG, I. H., and BUCHANAN, M. A., Color reaction of wood with methanolic hydrogen chloride, 191.
ISENBERG, I. H., BUCHANAN, M. A., and WISE, L. E., Extractives in American pulp woods, 347.
ISHIGURO, T. J., see Keimatsu.
— see Yoshiki.
ITERSON, G. VAN, Aerobic bacterial decomposition of cellulose, 112.
IVANOV, V. I., see Golova.
- J
- JACKSON, D. T., see Parsons.
JACKSON, E. L., and HUDSON, C. S., Oxidation of cellulose with periodic acid, 83, 278, 380.
— Formation of oxycellulose of the dialdehyde type by hypochlorite bleaching, 519, 529.
JACOBS, J. J., see Othmer.
JÄGER, R., see Unger.
JAHN, E. C., see Bloom.
— see Levy.
JAKOBSON, T., Bibliography of tall oil, 492.
JAKS, R., see Lieser.
JANCKE, W., see Herzog.
JANDEBEUR, W., see Schmidt.
JANDER, G., and SPANDAU, H., Determination of the molecular weight by dialysis, 223.
JANSON, A., see Freudenberg.
JAYME, G., Existence of lignin, 182.
— Utilization of hemicelluloses, 137.
— Pulping of isolated wood fibers, 490, 496.
— Bleaching of straw pulp with sodium chlorite, 402.
JAYME, G., and FINK, F., Pure cellulose content in spruce wood, 134, 150.
JAYME, G., and HANKE, G., Dissolution of a polysaccharide on chlorite treatment of spruce wood, 150.
— Protection of cellulose by lignin, 452, 471.
JAYME, G., and HARDERS-STEINHÄUSER, M., Tension wood, 25.
— Staining of wood cells, 193.
— Protection of cellulose by lignin, 451.
JAYME, G., and LOCHMÜLLER-KERLER, E., Rayon sulfite pulp from beech, 448.
— Relation between chemical composition, yield and strength of pulps, 452.
— Refined high-yield acid sulfite pulps from beech, 499, 504.
JAYME, G., and REH, F., Cellulose content in trees of different age, 133.
JAYME, G., and ROTHAMEL, L., Changes in the strength of beech pulp on bleaching with sodium chlorite, 452, 471.
— Bleaching of sulfate pulp, 524, 526, 528.
JAYME, G., SÄTRE, M., and MARIES, S., Oxidation of cellulose with periodic acid, 84.
JAYME, G., and SARTEN, P., Determination of pentosan, 144, 149, 178.
JAYME, G., and SCHORNING, P., Determination of "resistent pure cellulose", 133.
— Prehydrolysis of wood, 489.
JAYME, G., and WETTSTEIN, R., Wood fiber model, 452, 471.
JEANES, A., and ISELL, H. C., Oxidation of carbohydrates with chlorous acid, 524, 530.
JEGER, O., see Ruzicka.
JELLINEK, O., see Bergius.
JENKINS, S. H., see Norman.
JENNES, L. C., and NYSTROM, G. L., Sulfite semichemical pulping, 499, 504.
JENNINGS, W., Tall oil, 492.
JENSEN, W., Determination of lignin, 326.
— Sulfate cooking of hardwoods, 490, 496.
— Carbonization of wood, 538.
JODL, R., Difference between native and artificial humic acids, 554, 563.
— see Agde.
JØRGENSEN, L., Accessibility of cellulose, 61, 91.
JOHANSSON, AXEL, Colorimetric determination of furfural, 144.
JOHANSSON, ARVID, see Hägglund.
JOHANSSON, D., Relation of pulp quality to the wood character, 439.
— Relationship between pulp quality and springwood content of wood, 443.
— Sulfite pulping conditions and yield of ethyl alcohol, 459.
— Alkaline dry distillation of black liquor, 493.
— Kraft pulp from decayed wood, 561.
— see Hägglund.
JOHNER, H., see Staudinger.

- JOHNSEN, B., and LEE, H. N., Wood decay, 558.
- JOHNSON, A. M., and MARSHALL, H. B., Tanning agents from sulfite waste liquor, 465, 473.
- JOHNSON, M. J., see Wiley.
- see Leonard.
- JOHNSON, T., see Hägglund.
- JOHNSSON, E., see Enebo.
- JOHNSTON, H. W., and MAASS, O., Capillary holes in the pit membrane, 6.
- JONAS, K. G., Reaction of lignin with phenols, 185.
- Phenol lignin, 246.
- Biosynthesis of lignin, 320, 385.
- Formation of acetic acid during sulfite cooking, 456, 471.
- JONAS, K. G., and WALTER, P., Pulping with sulfurous acid, 437, 469.
- JONES, E. H. R., see Barton.
- JONES, E. J., Infrared spectrum of lignin, 210, 294.
- JONES, F. M., see Benson.
- JONES, J. K. N., see Hirst.
- JULLANDER, A., see Hägglund.
- JULLANDER, I., "Osmotic balance," 70.
- Determination of the molecular weight of nitrocelluloses, 70, 73, 168.
- Molecular weight distribution by "three parameter method," 75, 168.
- JULLANDER, I., and SVEDBERG, T., "Osmotic balance," 70, 168.
- JUNG, K. P., see Hess.
- JUNGKUNZ, J., see Pritzker.
- JURISCH, J., see Staudinger.
- K
- KAESZ, S., see Hamburger.
- KALB, L., Determination of lignin, 329, 330.
- KALB, L., and FALKENHAUSEN, F. v., Oxidation of cellulose with KMnO_4 , 83.
- KALB, L., PLESSMANN, F., and LORENTZ, H., Action of nitric acid on lignin, 270.
- KALB, L., and SCHOELLER, V., Determination of cellulose, 129.
- Phenol lignin, 246.
- KALB, L., see Willstätter.
- KALINOWSKY, W., Sulfolysis of cellulose 86, 170.
- KALLISTRATOFF, G. A., see Hodakoff.
- KARANOVIC, M., see Hägglund.
- KARATEJEW, A. W., Removal of methoxyl groups from lignosulfonic acid by chlorination, 226.
- KARGIN, V. A., and MICHAILOV, N. V., Stretching and crystallinity of cellulose, 65, 167.
- KARRER, P., Constitution of cellulose, 50, 164.
- Molecular size of cellulose, 64, 166.
- Classification of hemicelluloses, 134.
- KARRER, P., and BODDING-WIGER, B., Zinc dust distillation of hydrochloric acid lignin, 274.
- KARRER, P., and ESCHER, E., Alkylation of cellulose, 48.
- Methylation of cotton cellulose, 122.
- KARRER, P., and SCHUBERT, P., Action of snail enzymes on cellulose, 45, 163.
- KARRER, P., SCHUBERT, P., and WEHRLI, W., Action of snail enzymes on cellulose, 45, 163.
- KARRER, P., and WIDMER, F., Cellobiose, 42.
- Linkage of lignin with carbohydrates, 299.
- KARSTEN, F., see Pringsheim.
- KARVONEN, A., Purification of crude cymene, 457, 472.
- KAST, W., see Flaschner.
- KATZ, J. R., Micellar structure and the swelling of cellulose, 77.
- KATZEN, R., ARIES, R. S., and OTHMER, D. F., By-products from wood hydrolysis, 400, 412.
- KATZEN, R., and OTHMER, D. F., Partial hydrolysis of wood, 400.
- KATZEN, R., SAWYER, F. G., and OTHMER, D. F., Soluble lignin in hydrolyzed lignocellulose, 400, 412.
- KATZEN, R., see Olson.
- see Othmer.
- KAUFFMANN, H., Hypochlorite bleaching, 518.
- KAUFMANN, S., see Ruzicka.
- KAWAI, S., and SUGIYAMA, N., Egonol, 313, 384.
- KEFELI, T. Y., see Shorygina.
- KEILEN, I. I., and POLLAK, A., Alkali lignin as rubber filler, 260, 338.
- KEIMATZU, S., and ISHIGURO, T. J., Hinokinin, 340, 388.
- KEIMATSU, S., ISHIGURO, T. J., and YAMAMOTO, G., Tsugalactone, 322.
- KELLER, E. L., and MCGOVERN, J. N., Neutral sulfite semichemical pulping, 499, 504.
- KELLER, R., see Freudenberg.
- KELLY, W., see Haworth.
- KENYON, W. O., and YACKEL, E. C., Oxidation of cellulose with nitrogen tetroxide, 83, 169.
- KENYON, W. O., see McGee.
- see Taylor.
- see Unruh.
- see Yackel.
- KERENYI, E., see Waentig.
- KERN, E. J., see Wilson.
- KERN, W., Degree of polymerization of cellulose, 69, 167.

- KERP, W., and WÖHLER, P., Loosely bound sulfite, 429.
- KERR, T., and BAILEY, I. W., Secondary wall, 360.
- KERSTJENS, A. H., see Böeseken.
- KERTÉSZ, Z., Composition of sulfite turpentine, 457.
- KHAUTZ, I., see Kratzl.
- KIESEL, A., and SEMIGANOWSKI, N., Sulfolysis of cellulose, 100.
- KIESSIG, H., see Hess.
- KINELL, P. O., and RÄNBY, B. G., Polymolecularity of cellulose, 91.
- KING, E. G., see Hibbert.
- KINGSBURY, R. M., SIMMONDS, F. A., MILLS, R. T., and FENNEL, F. L., Bleaching of neutral sulfite semi-chemical pulp with sodium peroxide, 501, 505.
- KINGSBURY, R. M., see Simmonds.
- KIRCHNER, E., History of sulfite pulping, 414, 467.
- Relationship between wood quality and pulp quality, 438.
- Pulping of pine heartwood, 443.
- KIRMREUTHER, H., Fluorescence of sulfite pulps, 455, 471.
- KIURU, V., see Virtanen.
- KLAGES, F., Kinetics of cellulose hydrolysis, 97, 171.
- KLAR, M., Wood distillation, 531.
- KLASON, P., Lignosans, 40.
- Lignin content of spruce wood, 41.
- Definition of wood cellulose, 121.
- Determination of cellulose, 127.
- Galactose in sulfite waste liquor, 151, 178.
- Sugar in sulfite waste liquor, 156.
- Pentosans in spruce wood, 158.
- Heating of wood with aromatic amines or phenols, 186.
- Color reactions of wood, 187.
- Alcohol lignin, 194, 195, 237, 370.
- Sulfonation of lignin, 198, 199.
- Salting out of lignosulfonic acid, 218.
- Precipitation of lignosulfonic acid with aromatic amines, 219, 220, 372.
- Molecular weight of lignosulfonic acid, 223.
- Reaction of lignosulfonic acid with iodine, 226.
- Caustic fusion of lignin, 227, 374.
- Desulfonation of lignosulfonic acid with barium hydroxide, 228.
- Alkali lignin, 255.
- Sulfuric acid lignin, 263.
- Chemical linkage between lignin and carbohydrates, 297.
- Formation of lignin, 320.
- The rôle of light in the biosynthesis of lignin, 324.
- Determination of lignin, 324, 325.
- Alcohol soluble extractives from spruce wood, 336, 388.
- Determination of acetyl groups in wood, 349, 350, 389.
- Chemical composition of wood, 350.
- Loosely bound sulfite, 415, 467.
- "Burnt cook," 423, 468.
- Selenium content of cooking acids, 425.
- Determination of the pulping degree, 436.
- Sulfite turpentine, 457.
- Analysis of black liquor, 475.
- Sulfate pulping, 480.
- Wood distillation, 531, 532, 539.
- Formation of phenol during wood distillation, 534.
- KLASON, P., and BERGH, Å., Wood distillation, 533.
- KLASON, P., and EDLUND, T., Tannin content of spruce bark, 344.
- KLASON, P., and FAGERLIND, O., Alcohol lignin, 237, 375.
- Extraction of wood with hot water, 550, 552.
- KLASON, P., HEIDENSTAM, G. v., and NORLIN, E., Dry distillation of cellulose, 107.
- Wood distillation, 531.
- KLASON, P., and KÖHLER, J., Turpentine oil content of spruce wood, 333.
- Solubility of spruce resin, 336.
- KLASON, P., and SEGERFELT, B., Alkali lignin, 255.
- Borneol from fusel oil, 465.
- Sulfur distribution in black liquor, 480.
- KLATT, W., Determination of lignin, 328.
- KLAUDITZ, W., Degree of polymerization of wood cellulose, 123.
- Cellulose content of wood, 134.
- Links between cellulose and hemicelluloses, 141, 177.
- KLEINE, J., Polymolecularity and pulp quality, 68.
- KLEINERT, T., Phloroglucinol reaction of wood, 185, 369.
- KLEMM, P., Malachite green test, 436.
- KLINGSTEDT, F. W., Determination of pentosan, 143, 177.
- Determination of acetyl groups, 349.
- see Hägglund.
- KLINK, F., see Freudenberg.
- see Lautsch.
- KNACKSTEDT, W., see Schütz.
- KNOEVENAGEL, E., and BUSCH, H., Hydrocellulose, 78, 169.
- KNOPF, E., see Freudenberg.

- KOBE, K. A., LAYMAN, I. H., and ARM-
BRUSTER, F. R., Fertilizers from ligno-
sulfonic acid, 464, 473.
- KOCH, F., Xylan as constituent of wood
gum, 39.
— Wood gum, 138.
- KOCH, FR., see Bergius.
— see Hägglund.
- KOCH, H., Determination of mannan, 146.
— see Berl.
- KOCH, J. E., and KRIEG, W., Color
reagent for pine heart wood, 344, 388.
— Differentiation of heart and sapwood
from pine by color reaction, 445, 470.
- KOCH, K., see Eller.
- KOCH, W., Extraction of wood with hot
water, 550, 552.
- KÖGL, F., Auxines, 13, 27.
- KÖHLER, J., see Klason.
- KOELICHEN, K., Determination of the
hydroxyl ion concentration, 477.
- KÖNIG, F., Pulping with nitric acid, 270,
380.
— Oxidation of hydrochloric acid lignin
with ozone, 272.
- KÖNIG, J., Determination of cellulose,
126.
— Pulping with glycerol-sulfuric acid.
— Determination of lignin, 263.
— Incrustation theory, 297.
- KÖNIG, J., and BECKER, E., Galactan
from hardwoods, 152.
— Wood polyoses, 157.
— Determination of lignin, 327, 386.
— Analysis of German wood types, 350,
390.
- KÖNIG, J., and HÜHN, F., Phloroglucinol
reaction, 185, 369.
- KÖNIG, J., and RUMP, E., Pentosan con-
tent of acid lignins, 263.
— Incrustation theory, 298.
— Formation of lignin, 320.
— Determination of lignin, 327, 386.
- KÖNIG, J., see Skraup.
- KOERNER, T., Hydrolysis of cellulose with
hot mineral acids, 93, 171.
— Wood saccharification with dilute
acids, 392.
— Effect of oxidizing agents on wood
saccharification, 394, 411.
- KOHNSTAMM, P., Decomposition of wood
by *Merulius lacrimans*, 560.
- KOISTINEN, O., see Virtanen.
- KOLLMANN, F., Wood tissue, 27.
— Physical properties of wood, 36.
— Corrosion of wood, 552.
- KOMAROW, F., and FILIMONOWA, G., De-
composition of wood by microorga-
nisms, 559, 563.
- KOMPPA, G., and TALVITIE, Y., Composi-
tion of fusel oil, 462.
- KOON, C. M., see Hisey.
- KOSKULL, H. V., see Hägglund.
- KOSLOW, N. S., OLIPHSON, L. E., and
GOLDINA, S. M., Determination of
cellulose, 129.
- KOSSEL, W., Cellobiose, 42, 163.
- KRAEMER, E. O., Molecular dispersion of
cellulose in solutions, 69, 167.
- KRAEMER, E. O., and LANSING, W. D.,
Degree of polymerization of cellulose,
69, 167.
— Ultracentrifuge methods, 70, 168.
- KRAEMER, E. O., and NICHOLS, J. B.,
Ultracentrifuge methods, 70, 168.
- KRAFT, F., Chlorine consumption in
bleaching, 508, 514.
— Two-stage chlorination of pulp, 516,
521, 528.
— Decrease in viscosity during chlorina-
tion of pulp, 525, 528.
- KRAIS, P., Nitric acid pulping, 503.
- KRATKY, O., Micelle of the cellulose fiber,
56, 57, 165.
— Shape of the cellulose molecules, 76.
- KRATKY, O., BAULE, B., SEKORA, A., and
TREER, R., Stretching of hydrate cellu-
lose, 65, 167.
- KRATKY, O., and MARK, H., Shape of the
cellulose molecules in solution, 76.
- KRATKY, O., and SCHOSSBERGER, F.,
Dimensions of micelle and of the inter-
micellar spaces, 55.
- KRATKY, O., and SEKORA, A., Cellulose
micelles, 55, 165.
— Low-angle scattering, 59, 65.
- KRATKY, O., SEKORA, A., and TREER, R.,
Stretching of hydrate cellulose, 65,
167.
- KRATZL, K., Sulfonation of lignin models,
201, 237, 371, 374.
— Model experiments for vanillin for-
mation, 232, 234, 374, 375.
— Formation of acetaldehyde from ligno-
sulfonic acid, 232, 374.
— Biosynthesis of lignin in absence of
light, 324.
- KRATZL, K., and BLECKMANN, C., Eli-
mination of sulfur from lignosulfonic
acid by bromination, 227, 513.
- KRATZL, K., and DÄUBNER, H., Sulfona-
tion of chalcones, 200.
— Sulfonation of aromatic alcohols and
ketols, 202.
- KRATZL, K., DÄUBNER, H., and SIEGENS,
U., Sulfonation of lignin models, 201,
371.
- KRATZL, K., and KHAUTZ, I., Model
experiments for vanillin formation,
232, 374.

- KRATZL, K., and RETTENBACHER, F., Formation of acetaldehyde from lignosulfonic acid, 233, 375.
- KRATZL, K., see Wacek.
- KRAUSE, H., Galactose in sulfite waste liquor, 151, 178.
- Sugars in sulfite waste liquor, 156.
- Treatment of lignosulfonic acid with calcium hypochlorite, 226.
- KREIDER, L. C., see Gehman.
- KRESS, O., and VOIGTMAN, E. H., Decrease in viscosity during chlorination of pulp, 525, 530.
- The attack on pentosans and α -cellulose during chlorination of pulp, 526, 530.
- KRESS, O., HUMPHREY, C. J., RICHARDS, C. A., BRAY, M. W., and STADL, J. A., Utilization of decayed wood, 561, 564.
- KRESSMANN, F. W., Optimum conditions for wood saccharification with dilute acids, 392.
- see Sherrard.
- KRIEG, W., see Koch.
- KROHN, V., Yeast cultivation in sulfite waste liquor, 463.
- KRULL, H., Determination of lignin, 328, 386.
- Effect of oxidizing agents on wood saccharification, 394, 411.
- see Wohl.
- KRZEMIENIEWSKA, H., Aerobic cellulose bacteria, 112.
- KÜNG, A., Refractometric control of sulfite pulping, 436.
- KÜRSCHNER, K., Determination of cellulose, 129.
- Color reactions of wood, 187.
- Vanillin from sulfite waste liquor, 229.
- Sulfonation of lignin, 266, 379.
- Thermal decomposition of different lignin preparations, 268.
- Isolation of vanillic acid from decayed wood, 560.
- KÜRSCHNER, K., and HOFFER, A., Determination of cellulose, 129.
- KÜRSCHNER, K., and SCHRAMEK, W., Vanillin from sulfite waste liquor, 229.
- KÜRSCHNER, K., and WITTENBERGER, K., Indirect determination of lignin, 331.
- KÜSTER, W., and DAUR, R., Dioxane lignin, 244.
- KUETTEL, G. M., Phlobaphenes in kraft pulp, 488, 495.
- KÜTTNER, E., see Schramek.
- KUHN, E., see Eisenhut.
- KUHN, W., Constitution of cellulose, 45, 163.
- KUHN, W., Shape of the cellulose molecule in solution, 76.
- Kinetics of cellulose hydrolysis, 97, 171.
- see Freudenberg.
- KULKA, M., see Eastham.
- see Fisher.
- KULLGREN, C., Extraction of solid lignosulfonic acid with water and alcohol, 197, 226.
- Lignosulfonic acid in sulfite pulp, 216.
- Dissolution of lignosulfonic acid, 216, 421, 468.
- Ion-exchanging properties of sulfite pulp, 216.
- Kinetics of sulfite pulping, 421, 468.
- Change of alkalinity during alkaline pulping, 477.
- Sulfate pulping, 479, 480.
- KULLGREN, C., and DU RIETZ, C., Ion-exchanging properties of lignosulfonic acid, 216.
- KULLGREN, C., and TYDÉN, H., Determination of pentosans, 143.
- KURTH, E. F., Composition of essential oils and resins, 334, 335, 387.
- Chemical composition of barks, 358.
- KURTH, E. F., and RITTER, G. J., Easily hydrolyzable wood polyoses from spruce, 152.
- Fructan in white spruce, 153, 178.
- KURTH, E. F., see Ritter.
- KVORUP, K., see Späth.
- KYAME, L., see Fisher.
- L
- LACKEY, H. B., MOYER, W. W., and HEARON, W. M., Precipitation of condendrin from sulfite waste liquor, 342.
- LAGERBERG, T., Sulfite pulp from decayed heart wood, 562, 564.
- LAMARLIÈRE, L. G. DE, Mäule reaction, 193, 370.
- LAMM, O., Ultracentrifuge methods, 69, 168.
- LANE, H. C., Determination of the pulping degree, 436, 469.
- LANE, W. H., see Brauns.
- LANG, E. R., and LAURIN, E. T., Washing of bleached pulp with sodium metaphosphate, 518, 529.
- LANGE, G., Alkali lignin, 255.
- LANGE, P. W., Ultraviolet absorption and dichroism of lignin in the wood, 182, 293, 304.
- Ultraviolet absorption of lignin during sulfite pulping, 211, 424.
- LANGHANS, R., Wood saccharification, 410.
- LANGNER, W., Relative volumes of wood, water, and air in sapwood, 31.

- LANGWELL, H., Decomposition of cellulose by thermophilic bacteria, 113.
- LANSING, W. D., see Kraemer.
- LARIAN, M. G., see Mann.
- LAROCQUE, G. L., and MAASS, O., Velocity of soda pulping, 477.
- LARSON, L. L., Splitting of methoxyl groups on bromination of lignin, 512, 528.
- Elimination of sulfo groups by chlorination of lignosulfonic acid, 512.
- Chlorination of pulp, 508, 528.
- Splitting of a lignin-carbohydrate compound by chlorination, 517.
- LARSON, R., see Hägglund.
- LARSSON, A., Lignosulfonic acids from aspen, 223.
- Determination of lignin, 325, 385.
- see Gustavson.
- see Hägglund.
- LARSSON, E., Investigation of tall oil, 492.
- LASSETTIE, E. N., see Wolfrom.
- LAU, H., Hydrotropic dissolution of lignin, 261, 378.
- LAUER, K., Skin substance, 368.
- LAUGHLIN, E. R., see Lewis.
- LAURIN, E. T., see Lang.
- LAUTSCH, W., Pressure hydrogenation of lignin, 236, 275.
- Pressure hydrogenation of black liquor, 259, 494, 497.
- Anion exchangers from alkali lignin, 260, 465.
- Prehydrolysis and sulfite pulping of beech wood, 448.
- LAUTSCH, W., and PIAZOLO, G., Phenolic hydroxyl groups in lignosulfonic acid, 200, 371.
- Precipitation of lignosulfonic acid, 204, 220.
- Reductive breakdown of lignosulfonic acid, 237.
- Pressure hydrogenation of lignin, 237, 275, 380.
- Oxidation of brominated lignin, 280.
- Oxidation of iodinated lignin, 281, 381.
- Chlorine substitution in lignin, 512.
- LAUTSCH, W., PLANKENHORN, E., and KLINK, F., Alkaline oxidation of spruce wood in the presence of cobaltic hydroxide, 215.
- Pressure oxidation of lignosulfonic acid, 232.
- see Freudenberg.
- LAWRENCE, W. P., Chlorite bleaching, 524, 525, 530.
- LAYMAN, I. H., see Kobe.
- LEAF, R. L., JR., see Buchanan.
- see Pigman.
- LECHNER, R., Determination of pentosans, 143.
- LECHNER, R., and ILLIG, R., Condensation of aldehydes with barbituric acid, 188, 369.
- LECHNER, R., see Fink.
- LEE, H. N., Length of wood fibers, 20, 27.
- see Johnsen.
- LEEUW, A. J. DE, see Hermans.
- LEGELER, E., Phenol lignin, 248, 377.
- LEGER, F., see Hibbert.
- LEHMANN, F., see Beckmann.
- LEITCH, C. G., see Haworth.
- LEMAY, L., see Austerweil.
- LEMON, H. W., Ultraviolet absorption of phenols, 286, 381.
- LENEL, P. O., see Sohn.
- LENZE, F., PLEUS, B., and MÜLLER, J., Chemical linkage between cellulose and pentosans, 120, 174.
- Behavior of wood and cotton cellulose on nitration, 120, 174.
- Easily and difficultly hydrolyzable mannans, 145, 177.
- LEONARD, R. H., and HAJNY, G. J., Alcoholic fermentation of wood sugars, 399, 412.
- LEONARD, R. H., PETERSON, W. H., and JOHNSON, M. J., Lactic acid fermentation of sulfite waste liquor, 464.
- LEOPOLD, B., see Erdtman.
- LEVY, J., and JAHN, E. C., Chemical linkage between lignin and carbohydrates, 300.
- LEVY, M., see Terisse.
- LEWIS, H. F., By-products of sulfite pulping, 467.
- LEWIS, H. F., and LAUGHLIN, E. R., Speed of alkaline pulping, 476, 495.
- LEWIS, H. F., and RICHARDSON, C. A., Balloon formation of cellulose fiber in cuprammonium solution, 360.
- LEWIS, H. F., BRAUNS, F. E., BUCHANAN, M. A., and BROOKBANK, E. B., Meadol, 260.
- LEWIS, J. C., STUBBS, J. J., and NOBLE, W. M., Nutritive value of *Torula* yeast, 399, 412.
- LEWIS, J. C., see Brauns.
- LEWIS, S. J., Fluorescence of sulfite pulp, 455, 471.
- LIBBY, C. E., and O'NEIL, F. W., Chemi-groundwood pulp, 500.
- LICHTENSTADT, L., see Schroeter.
- LIEBHERR, F., see Späth.
- LIESCHE, O., see Beckmann.
- LIESER, T., Polymolecularity of cellulose, 64.
- Solubility of hydrocellulose in dilute alkali, 79.

- LIESER, T., and FICHTNER, F., Molecularly dispersed cellulose in water solution, 64, 166.
- LIESER, T., and JAKS, R., Molecularly dispersed cellulose in water solution, 64, 166.
- LIESER, T., JAKS, R., and GLITSCHER, E. A., Molecularly dispersed cellulose in water solution, 64, 166.
- LIESER, T., and SCHWIND, V., Chemical linkage between lignin and carbohydrates, 301.
- LIFSCHÜTZ, J., Determination of cellulose, 126.
- Nitric acid pulping, 503, 505.
- LINDBERG, B., see Erdtman.
- LINDBLOM, K., see Hägglund.
- LINDBERG, G., Formation of humus, 554, 563.
- LINDER, Å., see Skärblom.
- LINDGREN, B. O., Benzyl alcohols as lignin models, 202.
- Benzyl ethers as lignin models, 203, 209.
- Sulfite cooking of pinoresinol, 204.
- Chemistry of lignin sulfonation, 208.
- see Erdtman.
- LINDHOLM, I., see Hägglund.
- LINDSEY, J. B., and TOLLENS, B., Color reactions of wood, 187, 369.
- Sulfite waste liquor lactone (condendrin), 322.
- Fermentation of sulfite waste liquor, 431.
- Sulfite pulping, 415.
- LINDSEY, J. B., see Tollens.
- LINDSTRÖM, T., see Sandqvist.
- LINDVALL, E., see Bergek.
- LIONS, F., see Birch.
- LIPPMANN, E. O. V., Color reactions of wood, 183, 189, 369.
- LISSE, M. W., see Rose.
- LITTMANN, E., see Hilpert.
- LJUNGREN, S., see Hägglund.
- LÖBERING, J., Polymolecularity of rayon pulp, 68.
- LOCHMÜLLER-KERLER, E., see Jayme.
- LÖFMAN, N., see Hägglund.
- LÖFSTRÖM, P., see Hägglund.
- LÖSCHBRANDT, F., Bleaching of sulfate pulp, 514, 516, 517, 518, 528.
- LOFDAHL, L. J., see Harris.
- LOHMAN, H. J., see Schulz, G. V.
- LOLLAR, R. M., see Buchanan.
- LONGLEY, K. D., Fatty acid esters of lignosulfonic acid, 227.
- LORENZ, H., see Kalb.
- LORISCH, H., see Simon.
- LOTMAR, W., see Meyer.
- LOUGHBOROUGH, D. L., and STAMM, A. J., Molecular weight of lignin, 296.
- LOVELL, E. L., and GOLDSCHMID, O., Amorphous and crystalline regions in viscose fibers, 65.
- LOVELL, E. L., and HIBBERT, H., Fractionation of maple alcohol lignin, 243, 376.
- see Patterson.
- LOVIN, R. L., see Salvesen.
- LOWGREN, U., Defibrillation of wood, 105, 172.
- LÜDECKE, W., see Friese.
- LÜDTKE, M., Skin substance of cellulose fiber, 79, 364, 390.
- Sulfolysis of cellulose, 100, 172.
- Xylan in different wood elements, 140.
- Structure of fibers, 299.
- Primary and secondary lamella, 305.
- see Hess.
- LÜERS, H., Kinetics of the saccharification of cellulose dextrin, 94.
- Kinetics of acid hydrolysis of cellulose, 395.
- Wood saccharification, 411.
- LÜHRS, E., see Schlubach.
- LUNDBERG, A. H., Continuous semichemical pulping, 499, 504.
- LUNDIN, H., see Enebo.
- LYNCH, D. F. J., see Whittemore.

M

- MAAN, C. H., see Hermans.
- MAAS, H., see Hess.
- MAASS, O., CALHOUN, J. M., and YORSTON, F. H., Kinetics of sulfite pulping 421, 468.
- MAASS, O., CALHOUN, J. M., YORSTON, F. H., and CANNON, J. J. R., Kinetics of sulfite pulping, 421, 468.
- MAASS, O., see Campbell.
- see Johnston.
- see Larocque.
- see Macklin.
- MACFADYEN, A., and BLAXALL, F. R., Thermophilic cellulose fermentation, 110.
- MACGILLAVRY, D., Structure of the cellulose molecule, 50, 164.
- MACGREGOR, W. S., EVANS, T. H., and HIBBERT, H., C—CH₃ groups in lignin, 251, 316, 377.
- MACGREGOR, W. S., see West.
- MACHEMER, H., see Bergmann.
- see Haworth.
- MACKINNEY, H. W., see Hibbert.
- MACKLIN, L. S., and MAASS, O., Kinetics of soda pulping, 476, 495.
- MACMAHON, I. D., see Brennan.

- MACMILLAN, J. R., Bleaching of sulfate pulp, 510.
- MADSEN, J., Cellobiose, 42.
- MÄULE, C., Mäule reaction.
- MAHOOD, S. A., and CABLE, D. E., Pentosan content of different woods, 159.
— Determination of lignin, 327, 386.
— Chemical analysis of American woods, 352.
— Caustic fusion of wood, 541.
— Water-soluble material in wood, 550.
- MALCOLM, A. M., Industrial pulping with nitric acid, 504, 505.
- MALM, C. J., and FORDYCE, C. R., Cellulose phthalate, 49.
- MALM, E., see Björkman.
- MANN, C. H., MONTONNA, R. E., and LARIAN, M. G., Purification of crude cymene, 457, 472.
- MANNBRO, N., Neutralization of sulfite waste liquor 461.
— see Hägglund.
- MAQUENNE, L., and GOODWIN, W., Cellobiose, 42, 162.
- MARCHAND, R. F., Sulfolysis of cellulose, 86.
- MARCUSSEN, J., Coal formation, 553.
- MARCUSSEN, J., and PICARD, M., Dry distillation of wood, 534, 539.
- MARIES, S., see Jayme.
- MARION, L., see Hibbert.
- MARK, H., Strength of the main valency chain of cellulose, 116, 173.
— Distance between hydroxyl groups in cellulose, 53.
— Density of amorphous cellulose, 61, 166.
— Light scattering in polymer solutions, 75.
— Strength properties of high polymers, 525, 530.
- MARK, H., and FRILETTE, V. J., Reaction between deuterium and hydroxyl groups in cellulose, 60, 166.
- MARK, H., and MEYER, K. H., Dimensions of the cellulose micelle, 55, 165.
- MARK, H., see Badgley.
— see Brenner.
— see Goldfinger.
— see Hengstenberg.
— see Kratky.
— see Meyer.
— see Welch.
- MARKERT, L., see Freudenberg.
- MARSCHALL, A., Solubility of degraded cellulose, 85.
- MARSHALL, H. B., BRAUNS, F., and HIBBERT, H., Alkali lignin, 256, 285.
- MARSHALL, H. B., see Johnson.
- MARTIN, A. R., SMITH, L., WHISTLER, R. L., and HARRIS, M., Aldehyde end groups in cellulose, 81, 169.
- MARTIN, A. R., see Rutherford.
- MARTIN, G., Sulfate pulping, 481.
- MARTIN, J. S., see Borg.
— see Bray.
— see McGovern.
- MARTYNOV, M. F., Pulp yield from sulfite cooking, 420.
— Sulfite pulping of decayed wood, 561.
- MATHIESON ALKALI WORKS, Alkaline chlorine dioxide bleach, 522, 529.
- MATHIEU, M., see Desmaroux.
- MAUGHAN, M., see Peterson.
- MAURER, K., and REIFF, G., Oxidation of cellulose with nitrogen tetroxide, 83.
- MAXWELL, W., see Schulze.
- MAYR, H., Turpentine content of soft wood trees, 333.
- McBAIN, J. W., and SCOTT, D. A., State of cellulose in solutions, 64.
- McBEE, R. M., Thermophilic cellulose fermenting bacteria, 111.
- McCARTHY, J. L., HIBBERT, H., and TOMLINSON, G. H., Multistage bleaching, 521, 529.
- McCARTHY, J. L., see Cooke.
— see Creighton.
— see Daniels.
— see Godard.
— see Hewson.
— see Hiester.
— see Peniston.
— see Schwartz.
— see White.
- McCOY, E., see Wiley.
- McCOY, J. F., see Heuser.
- McCREADY, see Nolan.
- McCULLY, C. R., see Friedmann.
- McGEE, P. A., FOWLER, W. F., JR., and KENYON, W. O., Oxidation of cellulose with nitrogen tetroxide, 83, 169.
- McGEE, P. A., FOWLER, W. F., JR., TAYLOR, E. W., UNRUH, C. G., and KENYON, W. O., Oxidation of cellulose with nitrogen tetroxide, 83, 169.
- McGEE, P. A., see Taylor.
— see Unruh.
- McGOVAN, J. C., see Campbell.
- McGOVERN, J. N., Semichemical pulp in newsprint, 500, 505.
- McGOVERN, J. N., and DICKERMAN, G. K., Production of yeast from wood hydrolyzates, 399, 412.
- McGOVERN, J. N., EVERT, J. N., and CHIDESTER, G. K., Absorption of chemicals from neutral sodium sulfite liquors, 499, 504.

- McGOVERN, J. N., SCHAFER, E. R., and MARTIN, J. S., Bleaching of semi-chemical pulps, 501, 505.
- McGOVERN, see Chidester.
- see Keller.
- McGREAL, M. E., see Niederl.
- McKEE, R. H., Hydrotropic dissolution of lignin, 261.
- McKEEFE, E. P., and BRADLEY, L., The Keebra process, 498.
- McKEEFE, E. P., see Bradley.
- McKIBBIN, R. R., see Dyck.
- McNAUGHTON, G. C., see Chidester.
- McPHERSON, J., see Hasselström.
- McPHERSON, W. H., see Pigman.
- MEARS, J. S., see Carmody.
- MEESOOK, B., and PURVES, C. B., Determination of groups characteristic for oxycellulose, 85, 170.
- MEHTA, M. M., Pectin in the middle lamella, 154.
- Alkali lignin, 256.
- MEILER, J. G., Plastics from lignosulfonic acid, 466, 473.
- MEINEL, K., see Schmidt.
- MEISTER, M., see Freudenberg.
- MELANDER, K., Salting out of lignosulfonic acid, 219.
- Amine compounds of lignosulfonic acid, 220, 372.
- Molecular weight of lignosulfonic acid, 223.
- Caustic fusion of lignosulfonic acid, 227.
- MELSENS, G. F., Wood saccharification with dilute acids, 391.
- MENZIES, R. C., and DAVIES, A. E., Chlorine alkali pulping, 502, 505.
- MENZINSKY, G., Determination of mannose, 149, 178.
- Xylose and bisulfite, 431, 469.
- see Hägglund.
- MERLAU, O., see Heuser.
- MERRILL, D. R., see Scalione.
- MERRITT, R. W., and WHITE, A. A., Dry distillation of oak wood, 537.
- METZNER, U., see Schramek.
- MEYER, H., see Schütz.
- MEYER, K. H., Cellobiose model, 51, 164.
- K_m -constant in viscosimetry, 68, 167.
- Degree of polymerization of cellulose, 69, 167.
- Mercerization of cellulose, 77, 168.
- Hydrate cellulose, 77, 168.
- Strength of native cellulose fiber, 116, 173.
- Xylan, 141, 177.
- Pectins, 154, 179.
- MEYER, K. H., and BADENHUIZEN, N. P., Conversion of hydrate cellulose into native cellulose, 78, 168.
- MEYER, K. H., HOPF, H., and MARK, H., Constitution of cellulose, 45, 163.
- MEYER, K. H., and LOTMAR, W., Tensile strength of native cellulose fibers, 56, 165.
- MEYER, K. H., and MARK, H., Constitution of cellulose, 45, 163.
- Cross-linking of cellulose chains, 48.
- Model of the cellulose fiber, 55.
- MEYER, K. H., and MISCH, L., Unit cell of cellulose, 51.
- MEYER, K. H., see Mark.
- see Wyk, van der.
- MICHAILOV, N. V., see Kargin.
- MIE, G., see Staudinger.
- MILLER, R. N., see Rue.
- MILLS, R. T., see Kingsbury.
- MINOR, F. W., see Rutherford.
- MISCH, L., see Meyer.
- MITCHELL, C. A., Gallotannin reaction, 193.
- MITCHELL, R. L., Ultracentrifuge methods, 69, 168.
- Polymolecularity of wood carbohydrates, 123, 137.
- see Harris.
- see Ritter.
- see Rogers.
- MITSCHERLICH, A., Pectin fermentation, 110.
- Sulfite pulping, 435.
- High-yield acid sulfite pulping, 498.
- MITTERBILLER-EPP, J., Wood saccharification with concentrated sulfuric acid, 401.
- MOFFITT, J. E., SO_2 -washing after bleaching of pulp, 521, 529.
- MOILANEN, M., see Enkvist.
- MOLLE, T., Alkaloid content of roots of *Datura*, 347.
- MOLTER, H., see Freudenberg.
- MONIER-WILLIAMS, G. M., Sulfolysis of wood cellulose, 120.
- MONNBERG, R., Reductive breakdown of desulfonated lignosulfonic acid, 237.
- Chlorination of lignosulfonic acid, 227, 373.
- Pressure heating of lignosulfonic acid with methanol and lime, 467.
- MONSSON, W. H., see Curran.
- see Heritage.
- MONTONNA, R. E., see Haworth.
- see Mann.
- MOORE, A. B., JR., see Smith.
- MOORE, R. G. D., see Hibbert.
- MOORE, S. T., see Wise.
- MORGAN, R. A., see Walker.
- MORTON, T. H., see Cameron.

- MOSIMANN, H., Molecular weight determination of nitrocellulose, 70, 72, 169.
— Shape of the cellulose molecules in solution, 76.
- MOSIMANN, H., and SIGNER, R., Sedimentation-equilibrium method applied to nitrocelluloses, 70, 169.
- MOYER, W. W., see Lackey.
- MÜHLETHALER, K., see Frey-Wyssling.
— see Wuhrmann.
- MÜHLSTEDT, W., Dimensions of wood fibers, 23.
— Wood character and pulp strength, 439, 470.
- MÜLLER, F., Reagents for oxycellulose, 85, 170.
- MÜLLER, F. H., Shape of cellulose molecules in solution, 76.
- MÜLLER, H., Determination of cellulose, 126.
- MÜLLER, H. F., see Overbeck.
- MÜLLER, J., see Lenze.
- MÜLLER, O., Hexosan from beech wood, 151.
- MÜLLER, O., and BARTHOLME, M., Determination of lignin, 325, 385.
- MÜLLER, O., and STORCH, K., Determination of lignin, 325, 385.
- MÜLLER, R., Nitric acid pulping, 503, 505.
- MÜLLER, W. F., see Freudenberg.
- MÜNCH, E., Compression and tension wood, 25.
- MULDER, G. J., Determination of cellulose, 126.
— Pulping with nitric acid, 503.
- MUNTZ, A., Galactose in wood hydrolyzates, 39.
- MURDOCK, H. R., Sodium sulfite pulps (general survey), 501, 505.
- MUROMZEWA, W., see Scharkow.
- MURPHY, M., see Wise.
- MURUCHOW, J. J., see Tollens.
- N
- NAGAI, W., see Freudenberg.
- NÄGELI, C. v., and SCHWENDENER, S., The theory of micelles, 50.
- NAGEL, S. C., see Rue.
- NATHANSSON, A., Lignification and cell growth, 321, 385.
- NAUCK, W., Cellulose acetate, 120.
- NELSON, B., see Häggglund.
- NELSON, M. L., and CONRAD, C., Rate of hydrolysis and crystallinity of cellulose, 61, 166.
- NELSON, M. L., see Philipp.
- NETTHÖFEL, W., Hydrocellulose, 78, 169.
- NEU, E., Wood saccharification with hydrochloric acid, 410, 413.
- NEUBAUER, L. G., see Brandt.
- NEUBAUER, T., Light scattering of cellulose solutions, 76.
- NEUBERG, C., Hydrotropic solutions, 261.
- NEUBERG, C., and COHN, R., Formation of acetaldehyde in the bacterial decomposition of cellulose, 115.
- NEUENSTEIN, W. v., see Heuser.
- NEUMAN, J., Wood saccharification with dilute acids, 392, 396.
— Hydrolysis of cellulose with hot mineral acids, 93.
- NEUMANN, F., see Hess.
- NEUMANN, M., Indirect determination of lignin, 332.
- NEUMANN, P., see Rassow.
- NICHOLLS, R. V. V., see Burch.
- NICHOLS, J. B., see Kraemer.
- NICKEL, E., Color reactions of wood, 183, 187, 369.
- NICKERSON, A. W., Continuous high-yield pulping, 499, 504.
- NICKERSON, R. F., Oxidative hydrolysis of cellulose, 61, 65.
— Hydrolysis of cellulose with hydrochloric acid, 97, 171.
- NICKERSON, R. F., and HABRLE, I. A., Determination of crystalline and amorphous parts in cellulose materials, 61, 91.
- NIEDERL, J. B., SMITH, R. A., and McGREAL, M. E., Phenol lignin, 247, 377.
- NIEMANN, C., see Freudenberg.
- NIEMANN, J., see Borsche.
- NIEMEYER, D. D., see Forman.
— see Buchanan.
- NIGGEMANN, H., see Fischer.
- NIHLÉN, H., Two-stage sulfite cooking, 458, 472.
— see Häggglund.
- NIKKILÄ, O. E., see Virtanen.
- NILSSON, T., see Häggglund.
- NITTNER, E., see Wacek.
- NOBLE, W. M., see Lewis.
- NOERDLINGER, H., Separation of resin and fatty acids from tall oil, 491, 496.
- NOLAN, W. J., and MCCREADY, D. N., Kinetics of alkaline pulping, 476, 495.
- NOLL, A., Precipitants for lignosulfonic acid, 220.
- NOLL, A., and BOLZ, F., Determination of lignin, 327, 386.
- NOLL, A., BOLZ, F., and FIEDLER, H., Determination of lignin, 327, 386.
- NOLL, A., and HÖLDER, F., Determination of lignin, 327, 386.
- NORD, F. F., and VITUCCI, J. C., Formation of oxalic acid in wood decay, 115.
— Formation of methyl-p-methoxy-cinnamate, 116.

- NORD, F. F., see Schubert.
- NORDENSKJÖLD, J., Solubility of pine resin, 336.
- NORLIN, E., Dry distillation of wood, 533.
— see Klason.
- NORMAN, A. G., Aerobic cellulose decomposing bacteria, 112.
— Mechanism of cellulose fermentation, 114.
— Composition of xylan, 138, 176.
— Pectins, 154, 179.
— Determination of lignin, 264, 326.
- NORMAN, A. G., and JENKINS, S. H., Determination of Cross-Bevan-cellulose, 146.
— Determination of lignin, 327, 386.
- NORMAN, A. G., and NORRIS, F. W., Uronic acids in wood, 155, 179.
- NORMAN, A. G., and SHRIKHANDE, S. G., Pulping of silver fir with sodium sulfite and chlorine, 301.
- NORMAN, A. G., see Hawley.
- NORRIS, F. W., and PREECE, I. A., Fractional extraction of beech hemicelluloses, 140.
— Uronic acids in wood, 155, 179.
- NORRIS, F. W., see Norman.
- NORTON, G. S., Utilization of terpenes, 492, 497.
- NOWAK, P., see Schaarschmidt.
- NOWOTNOWNA, A., Mannan content of wood, 146, 178.
- NOYES, R. M., see Blaker.
- NYMAN, C., Evaporation of sulfite waste liquor, 429, 468.
— see Hägglund.
- NYSTROM, G. L., see Jenness.
- O
- ODÉN, S., Formation of lignin, 320, 385.
— Humic acids, 553, 562.
— see Wallin.
- ODINZOW, P. N., Effect of highly concentrated hydrochloric acid on wood, 265.
- O'DWYER, M. H., Composition of xylan, 138, 176.
— Galactan in hardwoods, 152, 178.
— Pectin from beech wood, 155.
— Alkaline extraction of oak wood, 155.
— Sugars in sulfite waste liquor, 159, 179.
- ÖGLAND, N. J., Dialysis of sulfite waste liquor, 224.
- ÖHGREN, T., see Samuelson.
- ÖMAN, E., Determination of pentosan, 143.
— Ion exchanging properties of sulfite pulp, 216.
— Sugars in sulfite waste liquor, 431, 469.
- Reddening of sulfite pulp, 454, 471.
- ÖRTENBLAD, T., Yields of cymene in sulfite cooking, 457, 472.
- ÖSTERLÖF, J., see Eng.
- OGAIT, A., Digestion of wood with chloral hydrate and mineral acids, 244.
- OLESKEVICH, V., SO₂-washing after bleaching, 521, 529.
- OLIPHSON, N. S., see Koslow.
- OLIVER, E., see Haworth.
- OLLEMAN, E. D., see Ritter.
- OLSON, E. T., KATZEN, R., and PLOW, R. H., Partial hydrolysis of wood, 400, 412.
- OLSON, E. T., and PLOW, R. H., Partial hydrolysis of wood, 400, 412.
- OLSON, F. R., Peterson, W. H., and SHERRARD, E. C., Bacterial decomposition of wood pulp, 115, 303.
- OMELIANSKI, W., Cellulose fermentation, 110.
- O'NEIL, F. W., see Libby.
- OPFERMANN, E., and HOCHBERGER, E., Hypochlorite bleaching, 518, 519, 529.
— Over-bleaching, 520, 529.
— Buffered bleaching, 520.
— The protective action of lignin during bleaching, 525, 530.
— Yellowing and hypochlorite bleach, 526, 530.
- ORMANDY, W. R. J., Wood saccharification with hydrogen chloride, 410, 413.
- OST, H., Cellobiose, 42.
— Cellotriose, 43.
— Reversion of glucose, 99, 171.
— Wood saccharification, 403.
- OST, H., and BRODTKORB, T., Hydrolysis of cellulose by hot mineral acids, 93, 171.
- OST, H., and WILKENING, L., Hydrolysis of cellulose by hot mineral acids, 93, 120, 171.
- OSTENBERG, Z., Wood saccharification, 410.
- OTHMER, D. F., GAMER, C. H., and JACOBS, J. J., Caustic fusion of sawdust, 542.
- OTHMER, D. F., JACOBS, J. J., and PABST, A. C., Caustic fusion of sawdust, 542.
- OTHMER, D. F., and KATZEN, R., Composition of wood tar, 535.
- OTHMER, D. F., and ROYER, R. H., Caustic fusion of sawdust, 542.
- OTHMER, D. F., see Katzen.
- OVERBECK, W., and MÜLLER, H. F., Pressure heating of wood with water, 105.
- OVERWIEN, T., see Schmidt-Nielsen.
- OWEN, L. N., see Hirst.

P

- PABST, A. C., see Othmer.
- PACSU, E., Mild hydrolysis of cellulose, 81.
Alkali sensitivity of the dialdehyde type of oxycellulose, 84.
Presence of highly acid-sensitive linkages in cellulose, 90.
Oxycellulose, 520.
see Hiller.
- PAERSCH, E., see Hillmer.
- PAJARI, K., Sterols from pine bark, 339.
- PALKIN, S., see Fleck.
- PALMER, E. C., By-products from wood distillation, 537.
- PALOHEIMO, L., Determination of lignin, 182, 368.
- PARSONS, J. L., and JACKSON, D. T., Hypochlorite bleaching, 518, 529.
- PASCOE, T. A., and SCHEFFER, T. C., Pulping of decayed wood, 562.
- PASCOE, T. A., see Borlew.
- PASTUCHOW, P. T., see Danilow.
- PATTERSON, R. F., and HIBBERT, H., Ultraviolet absorption of lignin, 292.
- PATTERSON, R. F., WEST, K. A., LOVELL, E. L., HAWKINS, W. L., and HIBBERT, H., Fractionation of maple alcohol lignin, 242, 376.
- PAUL, P. T., see Coleman.
- PAULING, L., Hydrogen bridges, 53.
- PAULY, H., Acetic and formic acid lignins, 247.
Iodination of lignin, 289.
Reaction of lignin with maleic acid anhydride, 289.
Molecular weight of lignin, 296.
- PAULY, H., and FEUERSTEIN, K., Chemical nature of hadromal, 184.
- PAVOLINI, T., Color reaction of wood with barbituric acid, 188.
- PAYEN, A., Cellulose from cell walls, 38, 181.
Reaction of wood with chlorine, 190.
Incrustation theory, 297.
Digestion of wood with 10 % hydrochloric acid, 391.
- PEAK, D. A., see Briggs.
- PEARL, I. A., Oxidation of spruce lignin, 280.
Oxidative breakdown of lignosulfonate, 235, 467.
Conidendrin from sulfite waste liquor, 342.
5-Hydroxymercurivanillin as slime controlling agent, 467.
- PEARL, I. A., and BENSON, H. K., Alkaline cleavage of lignosulfonic acid, 228.
- PEARL, I. A., BAILEY, A., and BENSON, H. K., Desulfonation of lignosulfonic acid with lime, 228, 374.
- PEAT, S., see Bywater.
— see Charlton.
- PEDERSEN, J. H., and BENSON, H. K., Removal of sulfo groups by chlorination of lignosulfonic acid, 226.
- PEDERSEN, K. O., see Svedberg.
- PEDERSEN, N., Formation of lignosulfonic acid, 415.
- PEDINELLI, M., and PESSARELLI, V., Colorimetric determination of furfural, 144, 177.
- PELIPETZ, M. G., Hydrotropic dissolution of lignin, 261, 378.
- PELOUZE, M. F., Wood saccharification with dilute acids, 391, 411.
Saccharification of cellulose, 402, 113.
- PENISTON, Q. P., and MCCARTHY, J. L., Phenolic hydroxyl groups in lignosulfonic acid, 200, 371.
Dialysis of sulfite waste liquor, 224.
Alkaline cleavage of lignosulfonic acid, 228.
- PENISTON, Q. P., MCCARTHY, J. L., and HIBBERT, H., Acetolysis of oak wood, 299.
- PENISTON, Q. P., see White.
- PENNINGTON, D. E., and RITTER, D. M., Molecular weight of lignosulfonic acids, 224, 297.
Periodate oxidation of ammonium lignosulfonate, 235.
Periodate oxidation of phenols, 236, 375.
- PENNINGTON, D. E., see Ritter.
- PEPPER, J. M., and HIBBERT, H., Phenolic products from hydrol lignin, 282.
- PERCIVAL, E. G. V., see Haworth.
— see Hibbert.
- PERRENOUD, H., Dioxane lignin, 244, 296.
- PERVIER, N. C., and GORTNER, R. A., Determination of pentosans, 143, 177.
- PESSARELLI, V., see Pedinelli.
- PETER, H., see Erbring.
- PETERS, O., see Hilpert.
- PETERSEN, C., and SCHÖDLER, F., Elementary composition of wood, 181, 368.
- PETERSON, F. C., BARRY, A. J., UNKAUF, H., and WISE, L. E., Arabogalactan, 152, 178.
- PETERSON, F. C., MAUGHAN, M., and WISE, L. E., Galactose and arabinose from *Larix occidentalis*, 151, 178.
- PETERSON, F. C., and SPENCER, C. C., Cellobiose, 42.
- PETERSON, F. C., see Freeman.
— see Wise.
- PETERSON, H. E., BRAY, M. W., and RITTER, G. J., Refined neutral sulfite semichemical pulps from fir, 499, 501, 504.

- PETERSON, W. H., and SNIESZKO, S., Bacterial decomposition of wood pulp, 303.
- PETERSON, W. H., SNELL, J. F., and FRAZIER, W. C., Fodder yeast from wood sugar, 399.
- *Torula* yeast from sulfite waste liquor, 463.
- PETERSON, W. H., see Leonard.
- see Olson.
- see Wiley.
- PETROV, N., Caustic fusion of hydrochloric acid lignin, 269, 379.
- PETERSON, G., Mitscherlich test, 435.
- PETTERSSON, T., see Erdtman.
- PEW, I. C., Taxifolin from Douglas fir heartwood, 346, 447.
- PFIRSCHKE, J., see Voss.
- PHELPS, M. W., and SCHUBER, I., Chlorination of pulp at elevated temperature, 512, 528.
- Washing of bleached pulp with lime, 517, 528.
- Decrease in viscosity during chlorination of pulp, 525, 528.
- PHILIPP, H. J., NELSON, M. L., and ZIFLE, H. M., Rate of hydrolysis and crystallinity of cellulose, 61, 166.
- PHILIPPOVICH, A. v., see Tropsch.
- PHILLIPS, J. B., see Hibbert.
- PHILLIPS, M., Decomposition of pine lignin by *Trametes pini*, 561.
- PHILLIPS, M., and GOSS, M. J., Zinc dust distillation of straw lignin, 258.
- Relation between the formation of lignin and plant growth, 321.
- PHILLIPS, M., GOSS, M. J., BROWN, B. E., and REID, F. R., Fertilizers from lignosulfonic acid, 464, 473.
- PIAZOLO, G., see Freudenberg.
- see Lautsch.
- PICARD, M., see Marcusson.
- PICTET, A., and GAULIS, M., Vacuum distillation of hydrochloric acid lignin, 268.
- PICTET, A., and SARASIN, J., Distillation of cellulose, 102, 106, 172.
- PICTET, R., and BRÉLAZ, G. L., Pulping with sulfurous acid, 437.
- PIGMAN, W. M., BROWNING, B. L., MCPHERSON, W. H., CALKINS, C. R., and LEAF, R. L., JR., Celluronic acids, 83, 169.
- PIGMAN, W. W., see Anderson.
- PLANKENHORN, E., see Freudenberg.
- see Lautsch.
- PLATZEK, P., see Hermans.
- PLESSMAN, F., see Kalb.
- PLEUS, B., see Lenze.
- PLOETZ, T., Determination of lignin, 264, 325.
- Enzymatic degradation of wood, 303.
- Prehydrolysis of wood, 489.
- see Freudenberg.
- PLÖTZE, E., see Husemann.
- PLOW, R. H., SAEMAN, J. F., TURNER, H. D., and SHERRARD, E. C., Wood saccharification, 398.
- see Olson.
- PLUNGUAN, M., Catalytic hydrogenation of Meadol, 258.
- PLUNGUAN, M., and HIBBERT, H., Humic acids, 554, 563.
- PODBREZNIK, F., Reactions of wood with aromatic amines and phenols, 186, 369.
- Phloroglucinol reaction of lignin, 188.
- POHJOLA, A., see Routala.
- POIROTS, G., see Fleury.
- POLANYI, M., Unit cell of cellulose, 50.
- POLANYI, M., and WEISSENBERG, K., Unit cell of cellulose, 50.
- POLLAK, A., see Keilen.
- POMILIO, U., Pulping with chlorine, 502, 505.
- POPOFF, A., Cellulose fermentation, 110.
- POSSOZ, L., Caustic fusion of wood.
- POTMĚŠIL, R., see Votoček.
- POTTER, G. J. C., and YORSTON, F. H., Dimensions of wood fibers, 23, 27.
- POUMARÉDE, J. A., and FIGUIER, L., Wood gum, 137.
- POWELL, W. J., and WHITTAKER, H., Determination of pentosans, 143, 177.
- Acetic acid lignin, 247.
- Elementary composition of alkali lignin, 257, 258.
- Nitration of alkali lignin, 260.
- POWERS, P. O., Utilization of terpenes, 492, 497.
- POWICK, W. C., Phloroglucinol color reactions, 188, 369.
- POWTER, N. B., Utilization of alkali lignin, 260, 378.
- PREECE, I. A., Fractionation of hemicelluloses of beech wood, 140.
- see Norris.
- PRELINGER, H., Water washing after alkaline extraction of bleached pulp, 518, 529.
- PRELL, E., see Pummerer.
- PREU, E., see Schwabe.
- PREY, V., see Suida.
- PRINGSHEIM, H., Enzymatic degradation of cellulose, 45, 114, 163.
- PRINGSHEIM, H., and ARONOWSKY, A., Cellulase and cellobiase, 45, 163.
- PRINGSHEIM, H., and FUCHS, W., Alkali lignin, 256.
- Bacterial decomposition of alkali lignin, 560.

- PRINGSHEIM, H., WEINREB, K., and KARSTEN, E., Hemicellulose, 134, 176.
- PRITZKER, J., and JUNGKUNZ, R., Determination of vanillin, 229, 374.
- PROCHOWNICK, V., see Schlubach.
- PROCTER, H. R., and HIRST, S., Precipitation of lignosulfonic acid with aromatic amines, 219.
- PROFFE, B., see Hägglund.
- PRÜTZ, G., see Huber.
- PUMMERER, R., PRELL, E., and HUPPMANN, G., Color of diphenylquinones in alkaline solution, 556.
- PURVES, C. B., see Assaf.
- see Gladding.
- see Harris.
- see Heidt.
- see Meesook.
- see Ritchie.
- see Wald.
- PURVIS, E. R., see Waksman.
- PYLE, J. J., see Brickman.

Q

- QUASEBARTH, K., see Schrauth.
- QVIST, W., Caustic fusion of wood, 541.

R

- RABINOV, G., see Heymann.
- RABINOWITSCH, B., see Hess.
- RACKY, G., Precipitation of lignosulfonic acid with fluorosilicic acid, 223.
- Composition of lignosulfonic acid, 285.
- RAFF, R. A. V., and TOMLINSON, G. H., 2ND, Alkali lignin as rubber filler, 260.
- RAMÉN, T., Evaporation of sulfite waste liquor, 429, 464, 468.
- RAMSAY, W., see Chorley.
- RÂNBY, B. G., Electron microscopy of hydrolyzed cellulose, 91.
- RÂNBY, B. G., and RIBI, E., Ultrasonic wave treatment of cellulose, 57.
- X-ray diffraction of hydrolyzed cellulose, 91.
- RÂNBY, B. G., see Bryde.
- see Banderet.
- see Gralén.
- see Kinell.
- RASHBACK, H., and YORSTON, F. H., Hypochlorite bleaching, 519, 529.
- RASSOW, B., and GABRIEL, H., Glycol lignin, 285.
- RASSOW, B., and NEUMANN, P., Glycol lignin from poplar wood, 243, 376.
- RASSOW, B., and WAGNER, K., Glycol lignin, 243.
- RASSOW, B., and ZICKMANN, P., Vacuum distillation of lignin, 268.
- Caustic fusion of hydrochloric acid lignin, 269, 379.

- Bromination of lignin, 272.
- Ether oxygen in lignin, 214, 372.
- Halogen uptake of lignin, 289, 381.
- RASSOW, B., and ZSCHENDERLEIN, A., Relationship between lignin and pentosans, 320.
- RATCLIFF, E. K., see Wise.
- RAU, H., see Freudenberg.
- RAWLING, F. G., and STAUDL, J. A., Semichemical pulp, 499, 504.
- RAWLING, F. G., see Rue.
- REEVES, R. E., SCHWARZ, V. M., and GIDDENS, J. E., Alcoholysis of cellulose, 97.
- REGESTAD, S. O., and SAMUELSON, O., Potentiometric titration of lignosulfonic acids, 225, 373.
- REH, F., see Jayme.
- REID, J. D., DRYDEN, E. C., and ARONOVSKY, S. I., The effect of monoethanolamine on lignin, 254.
- REID, J. D., see Whittemore.
- REID, F. R., see Phillips.
- REIFERSCHIEDT, E., Hydrolysis of cellulose by mineral acids, 93, 171.
- Wood saccharification with dilute acids, 392.
- REIFF, F., see Sohn.
- REIFF, G., see Maurer.
- REIN, H., see Hess.
- REINECKE, F., see Dolmetsch.
- see Staudinger.
- REISS, R., Formation of mannose on wood hydrolysis, 39, 162.
- RENKER, M., Determination of cellulose, 124, 125, 126.
- Reaction of wood with aniline, 186, 369.
- RENNERFELT, E., see Erdtman.
- RETTENBACHER, F., see Kratzl.
- RIBI, E., see Rânby.
- RICHARDS, C. A., see Hawley.
- see Kress.
- RICHARDSON, C. A., see Lewis.
- RICHARDSON, T., see Haworth.
- RICHTER, E., Resin content of wood, 335.
- Determination of the pulping degree, 436.
- RICHTER, G. A., Relationship of pulp quality to the cooking conditions, 449, 470.
- Sulfite pulping of hardwoods, 448.
- RICHTER, O., Phloroglucinol reaction of wood, 187.
- RICHTZENHAIN, H., Splitting of oxygen rings by sulfonation, 200, 318.
- Sulfite cooking of substituted aryl benzyl ethers, 203.
- Formation of stilbenes, 235.
- Oxidation of lignin with hydrogen peroxide, 272.

- Enzymatic oxidation of lignin models, 323.
- Metahemipinic acid from lignin preparations, 311.
- Oxidation of lignin and wood with permanganate, 311, 312.
- RICHTZENHAIN, H., and HOFE, C. v., 3,3'-Dimethoxy-4,4'-dihydroxystilbene from sulfite waste liquor of spruce, 235.
- RICHTZENHAIN, H., see Freudenberg.
- RIDGE, B. P., see Clibbens.
- RINGBOM, A., see Hågglund.
- RINGSTRÖM, E., see Björkman.
- RINMAN, E. L., Dry distillation of black liquor, 475, 493, 494.
- RITCHIE, P. F., and PURVES, C. B., Periodate lignin, 278.
- RITCHIE, P. F., see Wald.
- RITTENHOUSE, R. C., see Wise.
- RITTER, C. T., see Rogers.
- RITTER, D. M., PENNINGTON, D. E., OLLEMAN, E. D., WRIGHT, K. A., and EVANS, T. F., Structure of lignin, 200, 318.
- RITTER, D. M., see Pennington.
- RITTER, G. A., Semichemical pulping, 499, 504.
- RITTER, G. J., Dimensions of wood fibers, 23, 27.
- Isolation of pectin, 154.
- Lignin content of the middle lamella, 304.
- Removal of methoxyl during the isolation of lignin, 330.
- RITTER, G. J., and BARBOUR, J. H., Methoxyl content of spruce wood, 331.
- RITTER, G. J., and BIRD, C. D., Holo-cellulose, 136, 176.
- Acetyl groups in wood, 349, 389.
- Liberation of formic acid from wood, 350, 389.
- RITTER, G. J., and FLECK, L. C., Determination of cellulose, 125, 174.
- Pentosan content of different woods, 159.
- Chemical analysis of American woods, 352.
- Water-soluble material in wood, 550.
- RITTER, G. J., and KURTH, E. F., Holo-cellulose, 136.
- Acetyl groups in wood, 349, 389.
- Liberation of formic acid from wood, 350, 389.
- RITTER, G. J., and MITCHELL, R. L., Determination of cellulose, 125, 174.
- Uronic acids in wood, 155, 179.
- RITTER, G. J., see Kurth.
- see Peterson.
- ROBERTSON, G. I., see Irvine.
- ROBINSON, C. S., Corrosion of woods, 550.
- ROBINSON, G. M., and ROBINSON, R., Peltogynol, 346, 389.
- ROBINSON, R., and SMITH, H. G., Eudesmin, 341, 388.
- ROBINSON, R., see Robinson, G. M.
- RODEBUSH, W. H., see Buswell.
- ROE, R. B., Chlorine number, 419, 468.
- ROESCH, H., see Heuser.
- ROGERS, S. C., MITCHELL, R. L., and RITTER, C. T., Fractional alkaline extraction of wood polyoses, 155.
- ROGERS, S. C., see Harris.
- ROGUEIRO, B., see Fernández.
- ROLL, L. J., see Thurber.
- ROLLESTON, L. O., see Campbell.
- ROOS, E., see Staudinger.
- ROSCHIER, H., Determination of the pulping degree, 436.
- ROSE, R. E., and LISSE, M. W., Wood decay, 556.
- ROSENBLAD, C., Evaporation of sulfite waste liquor, 429, 464, 468.
- ROSENLUND, P., see Sieber.
- ROSENQVIST, T., see Hågglund.
- ROSEVEARE, W. E., see Welch.
- ROSS, J. H., Kinetics of soda pulping, 476, 495.
- see Adlington.
- ROSTEN, M. M., see Sankey.
- ROTH, J., see Austerweil.
- ROTH, L., see Gentzen.
- ROTHAMEL, L., see Jayme.
- ROUTALA, O., and POHJOLA, A., Composition of crude cymene, 457.
- ROUTALA, O., and SÉVON, J., Alcohol lignin, 238, 375.
- Acetic acid lignin, 248.
- Effect of nitric acid on hydrochloric acid lignin, 270, 380.
- Hydrogenation of lignin, 290, 382.
- Pulping with saltpeter and sulfuric acid, 503.
- ROUTALA, O., and VAUHKONEN, T., Formation of carbon dioxide during sulfite cooking, 457, 471.
- ROUTALA, O., and YLI-JAMA, O., Formation of carbon dioxide during sulfite cooking, 457, 471.
- ROWLEY, H. J., High-yield sulfite pulp for newsprint, 499, 504.
- see Hibbert.
- ROYER, R. H., see Othmer.
- RUE, J. D., Pulping with sodium sulfite, 498, 504.
- Addition of chlorine during chlorination of pulp, 507.
- Bleaching of sulfate pulp, 510, 516, 521, 528.
- Hypochlorite bleaching, 520, 528.

- Influence of temperature on hypochlorite bleaching, 521, 528.
 - Two-stage hypochlorite bleaching, 521, 528.
 - RUE, J. D., MILLER, R. N., and HUMPHREY, C. J., Industrial utilization of decayed wood, 561, 564.
 - RUE, J. D., and NAGEL, S. C., Bleaching of sulfate pulp, 521, 529.
 - RUE, J. D., and SCONCE, I. S., Bleaching of sulfate pulp, 510.
 - Chlorination of pulp, 510, 528.
 - Two-stage chlorination of pulp, 510, 528.
 - RUE, J. D., WELLS, S. D., RAWLING, F. G., and STAUDL, J. A., Semichemical pulp, 499, 504.
 - RUE, J. D., see White.
 - RUMP, E., see König.
 - RUNGE, F. F., Color reactions of wood, 183.
 - RUNIUS, S., see Holmberg.
 - RUNKEL, R., Morphology of wood fibers, 24.
 - RUNQUIST, L., see Hägglund.
 - RUSSEL, L. E., see Vincent.
 - RUSSELL, A., Structure of gymnosperm lignin, 200, 317.
 - RUSSELL, W. C., see Wise.
 - RUTHERFORD, H. A., and HARRIS, M., Oxidation of cellulose, 519, 529.
 - RUTHERFORD, H. A., MINOR, F. W., MARTIN, A. R., and HARRIS, M., Oxidation of cellulose with periodic acid, 84, 85.
 - RUTKOWSKI, R., see Hess.
 - RUZICKA, L., and BERNOLD, E., Agathidicarboxylic acid, 338, 388.
 - RUZICKA, L., BERNOLD, E., and TALLICHET, A., Agathidicarboxylic acid, 338, 388.
 - RUZICKA, L., and KAUFMANN, S., Abietic and levopimaric acids, 338, 388.
 - RUZICKA, L., and STERNBACH, L., Dextropimaric acid, 337, 338.
 - RUZICKA, L., STERNBACH, L., and JEGER, O., Abietic and levopimaric acids, 338, 388.
 - RUZICKA, W., see Hönig.
 - RYDHOLM, S., Hydrotropic dissolution of lignin, 262.
- S
- SAARNIO, J., see Sundman.
 - SABALITSCHKA, T., and DIETRICH, K. R., Indirect determination of lignin, 331, 386.
 - SACC, F., Dissolution of the mineral constituents of wood, 348, 389.
 - Pulping with nitric acid, 503, 505.
 - SACHS, J., Middle lamella, 17.
 - SACHSSE, R., Incrustation theory, 297.
 - SACK, J., see Tollens.
 - SAECHTLING, H., and ZOCHER, H., Swelling of spruce wood in different solvents, 36.
 - SAEGUSA, H., see Hachihama.
 - SAEMAN, J. F., Kinetics of cellulose hydrolysis, 96, 396, 397.
 - SAEMAN, J. F., BUBL, Z. L., and HARRIS, E. E., Saccharification of cellulose, 101.
 - SAEMAN, J. F., and HARRIS, E. E., Catalytic hydrogenation of methanol lignin, 246.
 - SAEMAN, J. F., LOCKE, E. G., and DICKERMAN, G. K., Wood saccharification, 399, 400, 411, 412.
 - Fodder yeast from sulfite waste liquor, 463.
 - SAEMAN J. F., see Harris.
 - see Plow.
 - SÄTRE, M., see Jayme.
 - SÄVÖ, G., see Hägglund.
 - SAKURADA, A., see Hess.
 - SALKOWSKI, E., Isolation of pentosans, 138, 176.
 - SALVESEN, J. R., HOSSFELD, R. L., and LOVIN, R. L., Reductive breakdown of lignosulfonic acid, 237.
 - Pressure heating of lignosulfonates with butanol-alkali, 237, 467.
 - SAMUELSEN, S., The course of bleaching, 507.
 - Chlorine demand for maximum brightness of pulp, 514.
 - SAMUELSEN, S., and HAUG, K., Hydrogen ion concentration in sulfite cooking liquor, 423, 468.
 - SAMUELSEN, S., see Heuser.
 - SAMUELSON, O., Potentiometric titration of lignosulfonic acid, 225.
 - Sulfate ions in sulfite cooking liquor, 427.
 - Loosely bound sulfite, 429.
 - Relationship between liquor color and pulp quality, 435, 469.
 - Polymolecularity and hypochlorite bleaching, 526, 530.
 - SAMUELSON, O., and ÖHGREN, T., Determination of sulfate ions, 427, 468.
 - SAMUELSON, O., and WESTLIN, A., Non-sulfonic acid sulfur in lignosulfonic acid, 225.
 - Thiosulfate and polythionates in sulfite waste liquor, 425.
 - SAMUELSON, O., see Björkman.
 - see Brunes.
 - see Gralén.
 - see Regestad.
 - SANDELIN, O., see Hägglund.
 - SANDERMANN, W., Lignoceric acid, 335.

- SANDERSON, T. F., see Harris.
- SANDQVIST, H., Composition of sulfate soap, 335.
- Phytosterol from tall oil, 492.
- SANDQVIST, H., and BENGTSSON, E., Phytosterol from tall oil, 492, 496.
- SANDQVIST, H., GORTON, J., and BENGTSSON, E., Phytosterol from tall oil, 492, 496.
- SANDQVIST, H., and HÖK, W., Sitosterol from tall oil, 492, 496.
- SANDQVIST, H., and LINDSTRÖM, T., Phytosterol from tall oil, 492, 496.
- SANDSTRÖM, G., and SANDSTRÖM, M., Fatty acids from tall oil, 491, 496.
- SANDSTRÖM, M., see Sandström, G.
- SANDSTRÖM, W. M., see Brink.
- SANKEY, C. A., and ROSTEN, M. M., Fermentation of sulfite waste liquor, 458, 472.
- SARASIN, J., see Pictet.
- SARKAR, P. B., Caustic fusion of jute lignin, 269, 279.
- Benzene polycarboxylic acids from lignin by pressure oxidation, 270, 380.
- Chlorination of hydrochloric acid lignin, 289, 381.
- Formaldehyde formation from hydrochloric acid lignin, 290.
- Acetyl groups in jute, 349.
- SARTEN, P., see Jayme.
- see Schütz.
- SAWYER, F. G., see Katzen.
- SCALIONE, CH. E., and MERRILL, D. R., Tannin content of redwood, 345.
- SCHAARSCHMIDT, A., NOWAK, P., and ZETZSCHE, W., Effect of nitrogen dioxide on hydrochloric acid lignin, 271.
- SCHACHT, W., Semi-Keebra process 499.
- SCHAEFER, C., see Erdmann.
- SCHAFER, E. R., see McGovern.
- SCHARKOW, W. I., and MUROMZEWA, W., Arabin and methyl pentosan content of Russian pine and birch wood, 352.
- SCHARTNER, H., see Emde.
- SCHEFFER, A., see Freudenberg.
- SCHEFFER, T. C., see Pascoe.
- SCHELHORN, F. B., see Wells.
- SCELLENBERG, H., Linkage between lignin and carbohydrates, 297.
- Lignin formation, 321, 385.
- SCHEUNERT, A., and WAGNER, K. H., Nutritive value of *Torula* yeast, 399, 412.
- SCHERER, A., see Heuser.
- SCHERRER, P., Crystal structure of ramie fiber, 50.
- see Debye.
- SCHIEBER, W., Polymolecularity of rayon, 68.
- Molecular weight of nitrated carbohydrates, 123, 174.
- SCHIEBOLD, E., Spatial arrangement of the macromolecules of cellulose, 54, 165.
- see Franz.
- SCHIEHMANN, W., Cellobiose, 42, 162.
- SCHILLER, H. v., see Semmler.
- SCHLEIDEN, M. J., Iodine-sulfuric acid reaction of cellulose, 38.
- Different "celluloses" in the cell walls, 39, 162.
- SCHLUBACH, H. H., Wood saccharification with dry hydrogen chloride, 411.
- SCHLUBACH, H. H., ELSNER, H., and PROCHOWNICK, V., Effect of hydrogen chloride at elevated pressure on cellulose, 101.
- Hydrochloric acid lignin, 267.
- SCHLUBACH, H. H., and LÜHRS, E., Treatment of glucose with dry hydrogen chloride at elevated pressure, 101.
- SCHLUBACH, H. H., and PROCHOWNICK, V., α -Glucosyl chloride, 101.
- SCHMIDHÄUSER, O., Strength of the cellulose fiber, 117.
- SCHMIDT, A., see Berl.
- SCHMIDT, E., End groups of the cellulose chain, 45.
- Sulfite pulping of pine wood, 444, 470.
- Delignification of wood with chlorine dioxide, 521.
- Action of chlorine dioxide on organic compounds, 523.
- SCHMIDT, E., ATTERER, M., and SCHNEGG, H., Galactan in the skeletal substance, 149, 152, 178.
- SCHMIDT, E., ATTERER, M., and THALER, H., Galactan in the skeletal substance, 152, 178.
- SCHMIDT, E., and GRAUMANN, E., Delignification with chlorine dioxide, 123, 174.
- Isolation of xylan from wood, 139.
- SCHMIDT, E., MEINEL, K., JANDEBEUR, W., and SIMSON, W., Acetyl, methoxyl, and carboxyl in hardwoods, 139, 176.
- Molecular size of xylans, 142, 177.
- SCHMIDT, E., MEINEL, K., NEVROS, K., and JANDEBEUR, W., Determination of pentosan, 143, 177.
- SCHMIDT, E., TANG, Y. C., and JANDEBEUR, W., Acetyl groups in xylan, 139, 176.
- SCHMIDT, E., and co-workers, Skeletal substance, 132, 175, 181, 368.
- SCHMIDT, G. E., SHERA, B. L., and TOOVEY, T. W., Alkaline extraction after bleaching, 517, 528.
- SCHMIDT-NIELSEN, S., Chlorination of pulp, 508, 514, 528.

- SCHMIDT-NIELSEN, S., and OVERWIEN, T.,
Velocity of alkaline pulping, 476, 495.
- SCHNEGG, H., see Schmidt.
- SCHNEIDER, G. G., and BOCK, H., Pectin
in wood, 154, 179.
- SCHNEIDER, W., see Fischer.
- SCHÖBERL, A., Behavior of organic disul-
fides on heating with alkali, 485, 495.
- SCHÖDLER, F., see Petersen.
- SCHOELLER, V., see Kalb.
- SCHOLLER, H., Kinetics of the sacchari-
fication of cellulose dextrin, 94.
— Kinetics of acid hydrolysis of cellu-
lose, 395.
— Wood saccharification, 396.
- SCHOPPACH, A., see Eller.
- SCHORGER, A. W., Xylan in wood, 138.
— Determination of mannan, 145.
— Pentosan content of different wood
types, 159.
— Mäule reaction, 193, 370.
— Zinc chloride reaction of wood, 193,
370.
— Linkage between lignin and carbo-
hydrates, 299.
— Constituents of turpentine, 334.
— Acetyl groups in wood, 349, 389.
— Chemical analysis of American woods,
352.
— Formation of acetic acid during wood
hydrolysis, 357.
— Fermentation of galactose, 393, 411.
— Sulfite turpentine, 457.
— Purification of crude cymene, 457,
472.
— Water-soluble material in wood, 550.
- SCHORGER, A. W., and SMITH, D. F.,
Galactan in spruce sulfite pulp, 151.
— Galactan in *Larix occidentalis*, 151.
- SCHORNING, P., see Hillmer.
— see Jayme.
- SCHOSSBERGER, F., see Kratky.
- SCHOTT, W., see Heuser.
- SCHRADER, H., see Fischer.
- SCHRAHEK, W., Crystallinity of fibers, 57.
— Xanthation of cellulose, 64.
- SCHRAHEK, W., and KÜTTNER, E.,
Xanthation of cellulose, 64, 166.
- SCHRAHEK, W., METZNER, U., and SEIDEL,
E., Wet strength of viscose rayon, 76.
- SCHRAHEK, W., and STENZEL, A., Dis-
solution of spruce cellulose fiber during
the viscose reaction, 359, 390.
— Structure of the cell wall, 365.
- SCHRAHEK, W., see Kürschner.
- SCHRAUTH, W., Structure of lignin, 237.
— Formation of lignin from carbohy-
drates, 320.
- SCHRAUTH, W., and QUASEBARTH, K.,
Phenol lignin, 246, 247, 377.
- SCHRENK, H. v., Decomposition of wood
by microorganisms, 558, 563.
- SCHRIMPF, A., Nitrocellulose, 120, 174.
— see Schwalbe.
- SCHROEDER, H., Ash content of different
parts of wood, 348.
- SCHROETER, G., LICHTENSTADT, L., and
IRINEU, D., Guaiaretic acid, 339, 388.
- SCHRYVER, S. B., see Candlin.
- SCHUBER, J., see Phelps.
- SCHUBERT, P., see Karrer.
- SCHUBERT, S., see Hönig.
- SCHUBERT, W. J., and NORD, F. F.,
Liberation of lignin in wood decay,
560.
- SCHULTÉN, K. AF, Chlorination of pulp.
- SCHULZ, G. V., Degree of polymerization
of cellulose, 69, 167.
— Sensitive linkages in cellulose, 89.
- SCHULZ, G. V., and HUSEMANN, E.,
Hydrolysis of cellulose with phos-
phoric acid, 89.
- SCHULZ, G. V., and LOHMANN, H. J.,
Hydrolysis of cellulose with phos-
phoric acid, 88.
- SCHULZ, G. V., see Husemann.
- SCHULZ, L., Nitrobenzene oxidation of
lignin and lignosulfonic acid, 231,
374.
- SCHULZ, W., see Schwalbe.
- SCHULZE, B., THEDEN, G., and VAUPEL,
O., Change of wood composition by
fungus attack, 559.
- SCHULZE, E., Cellulose and lignin, 38.
— Hemicellulose, 39, 134.
- SCHULZE, E., and GODET, C., Xylan from
seed hulls, 120.
- SCHULZE, E., STEIGER, E., and MAXWELL,
W., Galactose from wood, 39, 162.
- SCHULZE, F., Determination of cellulose,
126.
— Removal of incrusting substance,
181.
— Wood saccharification, 263.
— Incrustation theory, 297.
- SCHÜRENBERG, H., see Agde.
- SCHÜTZ, F., Pressure heating of wood
with water, 105.
— Pulping with glycerol, glycerol mono-
chlorohydrin and glycol chlorohydrin,
243.
— Pulping with monochloroacetic acid,
248.
— Extraction of wood with steam and
hydrogen peroxide, 182.
- SCHÜTZ, F., and KNACKSTEDT, W.,
Acetic acid lignin, 248.
- SCHÜTZ, F., and SARTEN, O., Pressure
heating of wood with water, 106.

- Reaction between wood and aromatic diazo compounds, 182.
— Refractive index of lignin, 295.
— Steam extraction of wood, 182.
- SCHÜTZ, F., SARTEN, P., and MEYER, H., Extraction of wood with steam and hydrogen peroxide, 182, 368.
- SCHWABE, K., and HAHN, E., Molecular weight of lignosulfonic acids, 223, 296, 372.
- SCHWABE, K., and HASNER, L., Molecular weight of lignosulfonic acids, 223, 296, 372.
- SCHWABE, K., and PREU, E., Addition of thiocyanogen to lignosulfonic acid, 227.
- SCHWALBE, C. G., Hydrolysis of different celluloses, 97.
— Treatment of sawdust with water under pressure, 105.
— Determination of cellulose, 126.
— Hemicellulose, 134, 176.
— Sulfite charcoal, 236.
— Sulfite pulping of pine heartwood, 443.
— Analysis of wood, 351.
— Semichemical pulp, 498, 504.
— Pulping with nitric acid, 503, 505.
— Decomposition of wood fiber through storage, 548.
- SCHWALBE, C. G., and BECKER, E., Solubility of pulp constituents in baryta water, 103.
— Methyl alcohol from wood, 154, 179.
— Relationship between lignin and pentosans, 385.
— Determination of lignin, 327, 386.
— Nitrogen and protein contents of different woods, 346.
— Acetyl groups in wood, 349, 389.
— Composition of some wood types, 351.
— Formation of acetic acid in sulfite pulping of hardwoods, 457, 471.
- SCHWALBE, C. G., and BERLING, K., Sulfite charcoal, 236, 375.
- SCHWALBE, C. G., and EKENSTAM, A. AF, Sulfite pulping of pine heart wood, 444.
- SCHWALBE, C. G., and FELDTMANN, G. A., Glucuronic acid from straw, 155.
- SCHWALBE, C. G., and GRIMM, H., Resin content of wood, 335, 387.
- SCHWALBE, C. G., and HAGSTRÖM, N. F., Semichemical pulp, 498.
- SCHWALBE, C. G., and SCHRIMPF, A., Nitrocellulose, 120, 174.
- SCHWALBE, C. G., and SCHULZ, W., Resins and fats in wood, 335, 387.
- SCHWARTZ, H., MCCARTHY, J. L., and HIBBERT, H., Reddening of sulfite pulp, 454, 471.
- Water soluble lignin in black liquor, 488.
— Lignin compounds in sulfate pulp, 506, 528.
- SCHWARTZ, H., see White.
- SCHWARTZ, S. L., and BRAY, M. W., Kinetics of alkaline pulping, 476, 495.
- SCHWARTZ, S. L., see Bray.
- SCHWARZ, V. M., see Reeves.
- SCHWENDENER, S., see Nägeli.
- SCHWIND, V., see Lieser.
- SCONCE, I. S., see Rue.
- SCOTT, A., see Brown.
- SCOTT, D. A., see McBain.
- SEARS, G. R., Electron microscopy of cellulosic materials, 57.
- SEDLITZKI, J. D., Aromatic nature of humus, 554.
- SEGERFELT, B., see Klason.
- SEIDEL, E., see Schramek.
- SEKORA, A., see Kratky.
- SELIWANOFF, TH., Color reactions of wood, 187, 188.
- SEMB, J., see Stamm.
- SEMIGANOWSKI, N., see Kiesel.
- SEMLER, F. W., and SCHILLER, H. V., Carene in pine-needle oil, 333, 387.
- SENF, M., Wood carbonization, 533.
- SEVÓN, J., Commercial preparation of chlorine dioxide, 521, 529.
— see Routala.
- SHARMA, F. D., Mäule reaction, 193, 370.
- SHAW, A. C., see Burch.
- SHELDRIK, G., see Haworth.
- SHEMA, B. F., see Heuser.
- SHERA, B. L., see Schmidt.
- SHEREBOW, L. P., Formation of lignin, 321, 385.
- SHERARD, E. C., Fermentation of galactose, 393.
- SHERARD, E. C., and AIYAR, S. S., Composition of spruce cellulose, 119.
- SHERARD, E. C., and BEGLINGER, E., Wood saccharification with dilute sulfuric acid, 400, 412.
- SHERARD, E. C., BEGLINGER, E., HOHF, F. P., and BATEMAN, E., Wood saccharification with dilute sulfuric acid, 400, 412.
- SHERARD, E. C., and BLANCO, G. W., Composition of spruce cellulose, 119.
— Fructan from white spruce, 153.
— Hemicelluloses in white spruce, 157.
— Wood saccharification with dilute acids, 393.
- SHERARD, E. C., and FROEHLKE, A. W., Acid hydrolysis of cellulose, 99.

- SHERRARD, E. C., and GAUGER, W. H., Catalysis in wood saccharification, 394, 396.
- SHERRARD, E. C., and HARRIS, E. E., Sulfuric acid lignin, 263, 378.
- SHERRARD, E. C., and KRESSMAN, F. W., Wood saccharification, 395.
- SHERRARD, E. C., see Anderson.
- see Harris.
- see Olson.
- see Plow.
- SHIMODA, J., Nitrogen dioxide pulping, 503.
- SHOCKLEY, W., see Heuser.
- SHORUIGIN, P. P., and SMOLYANINOVA, E. K., Vanillin from sulfite waste liquor, 229, 374.
- SHORYGINA, N. N., and KEFELI, T. Y., Cuproxam lignin, 278.
- SHRIKHANDE, S. G., see Norman.
- SIEBER, R., Determination of cellulose, 125, 175.
- Determination of lignin, 327, 386.
- Resin content of wood, 335.
- SIEBER, R., and ROSENLUND, P., Determination of lignin, 327, 386.
- SIEBER, R., see Heuser.
- SIEGENS, U., see Kratzl.
- SIGGIA, S., see Goldfinger.
- SIGNER, R., and GROSS, H., Determination of the polymolecularity of cellulose, 69, 168.
- SIGNER, R., see Mosimann.
- see Staudinger.
- SIITOLA, H., Velocity of the decomposition of cellulose in zinc chloride solutions, 90.
- SILLÉN, L. G., Degradation of high polymer chains, 89.
- Evaporation of sulfite waste liquor, 428.
- see Eng.
- SIMMONDS, F. A., and KINGSBURY, R. M., Bleaching of semichemical pulps, 501.
- SIMMONDS, F. A., see Arnold.
- see Kingsbury.
- SIMON, O., and LORISCH, H., Determination of cellulose, 126.
- SIMONSEN, E., Hydrolysis of cellulose by hot mineral acids, 92.
- Wood saccharification with dilute acids, 391.
- SIMSON, W., see Schmidt.
- SINGER, B., see Bray.
- SINGER, M., Vanillin and coniferin in wood, 187.
- SISSON, W. A., X-ray examination of celluloses, 65.
- "Mixed crystallization" between cellulose and non-cellulosic constituents, 141, 177.
- SKÄRBLÖM, K., and LINDER, Å., Terpenes from sulfate turpentine, 492, 497.
- SKEWES, T. S., and BENSON, H. K., Oxalic acid from lignosulfonic acid, 227, 374.
- SKJÖLDEBRAND, C., see Heuser.
- SKRAUP, Z. H., and KÖNIG, J., Cellobiose acetate, 42.
- SMITH, C., Furfuroids in straw and esparto, 161, 180.
- see Cross.
- SMITH, D. F., see Schorger.
- SMITH, E. H., MOORE, A. B., JR., and CHESLEY, K. C., Water wash after alkaline extraction in bleaching, 518, 529.
- SMITH, H. G., Gmelinol, 341, 388.
- see Robinson.
- SMITH, L., see Martin.
- SMITH, R. A., see Niederl.
- SMITH, W. H., Action of sunlight and ozone on wood, 549.
- see Waksman.
- SMITHEY, I. W., see Wheeler.
- SMOLYANINOVA, E. K., see Shoruigin.
- SNELL, J. F., see Peterson.
- SNIESZKO, S., see Peterson.
- SOBEK, A., see Freudenberg.
- SOFF, K., see Freudenberg.
- SOHN, A. W., Reductinic acid from wood hydrolyzates, 155.
- SOHN, A. W., and LENEL, P. O., Formation of reductinic acid, 155, 179.
- SOHN, A. W., and REIFF, F., Pulping with sodium chlorite, 503.
- SOHNS, F., see Freudenberg.
- SONDERHOFF, R., see Burgstaller.
- SOOKNE, A. M., and HARRIS, M., D. P. and strength of rayon, 69.
- SORKIN, M., see Staudinger.
- SOUCI, S. W., Humic acids, 553, 662.
- SOWDEN, J. C., see Wolfrom.
- SPANDAU, H., and GRIESS, W., Determination of molecular weight by dialysis, 223.
- SPANDAU, H., see Jander.
- SPÄTH, E., and KVORUP, K., Synthesis of pinosylvlin, 344, 389.
- SPÄTH, E., and LIEBHERR, F., Synthesis of pinosylvlin, 344, 389.
- SPECHT, H., see Bergius.
- SPEISER, R., and EDDY, C. R., Pectins in wood, 154, 179.
- SPEISER, R., EDDY, C. R., and HILLS, C. H., Pectins in wood, 154, 179.
- SPENCE, G. K., Effect of sulfur in soda pulping, 488, 496.
- SPENCER, C. C., see Peterson.
- SPITZER, J., see Hönig.
- SPONSLER, O. L., and DORE, W. H., Diameter of the hexose molecule, 50.

- SPROUT, O. S., JR., and TOOVEY, T. W., Chlorination of pulp, 514, 528.
- Two-stage chlorination of pulp, 516, 528.
- SPURLIN, H. M., Distribution of substituents in alkylcelluloses, 63.
- STACH, R., Relation between humic substance and lignin, 556.
- STADLER, R., see Grassmann.
- STADL, J. A., see Kress.
- see Rawling.
- see Rue.
- see Wells.
- STAMM, A. J., Surface properties of wood, 36.
- Osmotic measurements of cellulose derivatives, 70.
- Ultracentrifuge methods, 70.
- STAMM, A. J., and COHEN, W. E., Molecular weight of cellulose, 87, 170.
- STAMM, A. J., and HANSEN, L. A., Specific weight of wood, 31.
- STAMM, A. J., SEMP, J., and HARRIS, E. E., Chemical nature of lignin, 293.
- STAMM, A. J., see Loughborough.
- STANIER, R. Y., Aerobic cellulose bacteria, 112.
- STAUDINGER, H., Swelling of high-polymers, 36.
- Wood polyoses, 40.
- Constitution of cellulose, 45.
- Carboxyl groups in cellulose, 45, 163.
- Cellulose solutions, 66.
- Polyoxymethylene, 67.
- Viscosity of solutions of linear molecules, 68.
- Tearing strength and degree of polymerization, 69.
- Kinetics of cellulose hydrolysis, 88.
- Formic acid lignin, 248.
- Relation between length of the cellulose chain and pulp strength, 453.
- Degree of polymerization of wood cellulose, 453.
- STAUDINGER, H., and DAUMILLER, G., Cellulose xanthate, 64, 166.
- STAUDINGER, H., and DREHER, E., Decomposition of cellulose by mechanical means, 117.
- Degree of polymerization of wood cellulose, 122.
- Viscosity of sodium lignosulfonate, 224.
- Formic acid lignin, 252, 284, 296.
- Mechanical degradation of cellulose, 453.
- STAUDINGER, H., DREHER, E., and EKENSTAM, A. AF, Extractability of cellulose from wood, 300, 383.
- STAUDINGER, H., DREHER, E., and JURISCH, F., Degree of polymerization of wood cellulose, 122, 174.
- STAUDINGER, H., and EDER, K. J., Determination of the end groups of degraded celluloses, 45.
- Degradation of cellulose in cuprammonium solutions, 84.
- STAUDINGER, H., HERRBACH, P., and STOCK, H., Solubility of cellulose derivatives and differences between the cellulose of different plants, 65.
- STAUDINGER, H., and HEUER, W., Viscosity of sol and gel solutions, 69, 168.
- STAUDINGER, H., and HUSEMANN, E., Cellulose content of wood, 131.
- Degree of polymerization of wood cellulose, 133.
- Nylan, 142, 177.
- Cellulose content of spruce wood, 356.
- STAUDINGER, H., JOHNER, H., SIGNER, R., MIE, G., and HENGSTENBERG, J., Viscosity of solutions of linear molecules, 67, 167.
- STAUDINGER, H., and JURISCH, J., Degree of polymerization of very old cellulose materials, 81.
- Oxycellulose, 82.
- STAUDINGER, H., and REINECKE, F., Wood polyoses, 135.
- Relationship between degree of polymerization and strength of fiber, 453, 471.
- STAUDINGER, H., and ROOS, E., Mild oxidation of cellulose, 83.
- STAUDINGER, H., and SIGNER, R., Macromolecule lattice of cellulose, 56, 165.
- STAUDINGER, H., and SORKIN, M., Effect of acids on native cellulose, 80.
- Strength of degraded cellulose fibers, 117.
- α -Cellulose, 453, 471.
- STAUDINGER, H., and ZAPP, F., Cellulose xanthate, 64, 166.
- STAUDINGER, M., Separation of wood polyoses and cellulose from lignin, 305.
- STEENBERG, B., Balloon swelling of beaten fibers, 360.
- STEEVES, W. H., and HIBBERT, H., Acetylation of oak wood, 196.
- STEIGER, E., see Schulze.
- STEIN, R. S., and DOTY, P. M., Cellulose acetate in acetone solution, 75.
- STEINBRUNN, G., see Freudenberg.
- STENZEL, A.-L., see Schramek.
- STERN, A. L., Cellulose disulfuric acid, 86.
- STERNBACH, L., see Ruzicka.

- STEURER, E., Degradation of cellulose in oscillating beater, 118.
— see Hess.
- STILES, W., Trace elements in wood, 349, 389.
- STILLINGS, R. A., and BROWNING, B. L., Colorimetric determination of furfural, 144, 177.
- STIX, W., see Fuchs.
- STOCK, E., see Tschirch.
- STOCK, H., see Staudinger.
- STOCKMAN, L., Reaction between formic acid and bisulfite, 425, 433.
- STOCKMAN, L., and HÄGGLUND, E., Polyoses from spruce wood, 139, 142, 148, 156.
— Composition of spruce wood, 356, 390.
— Composition of compression wood, 357.
- STOCKMAN, L., see Hägglund.
- STOECK, G., see Friese.
- STÖCKLY, J. J., State of cellulose in solutions, 64.
- STORCH, K., Dioxane lignin, 244, 285.
— Wood decay, 561.
— see Müller.
- see Wedekind.
- STORIN, G. K., see Casciani.
- STREEB, E., Alkali lignin, 255.
- STREHLENERT, R. W., Sulfite charcoal, 236.
- STRICKER, F., see Hess.
- STRITAR, M. J., see Zeisel.
- STUBBS, J. J., see Lewis.
- STUDER, M., see Wyk, van der.
- STUMPF, W., and FREUDENBERG, K., Dioxane lignin, 297.
- SUGIYAMA, N., see Kawai.
- SUIDA, H., and PREY, V., Pressure heating of acid lignin, 269.
- SUIDA, H., and TITSCH, H., Methylation of wood, 299, 383.
- SUMMONDS, F. A., see Billington.
- SUNDMAN, J., Fructose in sulfite waste liquor and wood, 153.
— Hexoses in sulfite waste liquor, 156.
— Loosely bound sulfite, 429.
- SUNDMAN, J., SAARNIO, J., and GUSTAFSSON, C., Xylose and arabinose in hydrolyzates of wood, 159.
- SUNDROOS, B., see Hägglund.
- SUNESSON, E. B. F., Bleaching of sulfate pulp, 510.
— see Holmberg.
- SUTERMEISTER, E., Consumption of alkali during alkaline pulping, 476, 494.
— Cooking conditions and bleachability of sulfate pulp, 515, 528.
— Water-soluble material from mechanical pulp, 550.
- SVEDBERG, T., Determination of the polymolecularity of cellulose, 69, 168.
— "Osmotic balance," 70.
- SVEDBERG, T., and PEDERSEN, K. O., Ultracentrifuge methods, 69, 168, 296, 383.
— see Gralén.
- see Jullander.
- SWARTZ, J. N., see White.
- SWOBODA, O., see Wurz.

T

- TAKEMURA, W., see Hachihama.
- TALLICHET, A., see Ruzicka.
- TALVITIE, Y., see Komppa.
- TANG, Y. C., Acetyl groups in wood, 349.
— see Schmidt.
- RASMAN, H. E., and COVEY, A. J., Ultracentrifuge methods, 69, 168.
- TAUBER, I., see Wedekind.
- TAUSS, H., Decomposition of cellulose with alkali, 102.
— Extraction of wood with hot water, 550, 552.
- TAYLOR, E. W., FOWLER, W. F., JR., MCGEE, P. A., and KENYON, W. O., Oxidation of cellulose with nitrogen tetroxide, 83, 169.
- TAYLOR, E. W., see McGee.
- TAYLOR, M. C., WHITE, J. F., and VINCENT, G. P., Chlorite bleaching, 523, 530.
— Activation of chlorites with hypochlorite, 523, 530.
— Bleaching and oxidation potentials, 525, 530.
- TAYLOR, M. C., WHITE, J. F., VINCENT, G. P., and CUNNINGHAM, G. M., Sodium chlorite, properties and reactions, 503, 505.
— Activation of chlorites with hypochlorites, 523, 530.
- TAYLOR, M. C., see White.
- TEMNIKOWA, T. J., α -Hydroxypropionguaiacone, 241, 376.
- TERISSE, H., and LEVY, M., Wood saccharification with hydrochloric acid, 409.
- THALER, H., see Schmidt.
- THEDEN, G., see Schulze.
- THENARD, L. J., see Gay-Lussac.
- THIEME, R. J., see Coster.
- THIERSCH, F., Kinetics of the acid hydrolysis of cellulose, 396.
- THIESSEN, R., Fringe micelle, 57, 165.
— State and distribution of lignin in wood, 305.
- THOMSEN, T., Wood gum, 39, 137.

- THORN, W., Wood saccharification with dilute acids, 391.
 — Caustic fusion of wood, 540.
- THURBER, F. H., and ROLL, L. J., Terpenes, 334.
- TIEMANN, F., Cinnamaldehyde hydrosulfonic acid, 201, 371.
- TIEMANN, F., and HAARMANN, W., Coniferin in cambial sap of conifers, 319.
- TILGHMAN, B. C., Pulping with sulfurous acid or calcium bisulfite, 414, 436, 498.
- TIMELL, T., Amorphous and crystalline material in celluloses, 60, 62.
 — Distribution of substituents in methylcellulose, 63.
- TINGLE, A., Indirect determination of lignin, 331.
- TITSCH, H., see Suida.
- TOBEL, G. ZUM, see Weltzien.
- TOBLER, F., Formation of lignin, 321.
- TOLLENS, B., Definition of cellulose, 41.
 — Mannan in wood, 144.
- TOLLENS, B., and DMOCHOWSKY, R., Determination of cellulose, 126.
- TOLLENS, B., and LINDSEY, J. B., Galactose in sulfite waste liquor, 151, 178.
 — Isolation of lignosulfonic acid, 218.
 — Bromination of lignosulfonic acid, 226.
- TOLLENS, B., MURUCHOW, J. J., and SACK, J., Hydrocellulose, 78, 169.
- TOLLENS, B., SACK, J., and MURUCHOW, J. J., Solubility of degraded cellulose in calcium hydroxide solution, 103.
- TOLLENS, B., and TROMP DE HAAS, R. W., Pulping with nitric acid, 503.
- TOLLENS, B., see Browne.
 — see Cross.
 — see Gans.
 — see Lindsey.
 — see Wheeler.
- TOMLINSON, G. H., Magnesium bisulfite pulping, 437, 469.
- TOMLINSON, G. H., and WILCOXSON, L. S., Magnesium bisulfite pulping, 437, 469.
- TOMLINSON, G. H., see Ewen.
- TOMLINSON, G. H., 2ND, Model experiments on vanillin formation, 232, 374.
- TOMLINSON, G. H., 2ND, and HIBBERT, H., Vanillin from sulfite waste liquor, 229.
 — Alkaline cleavage of lignosulfonic acid, 228.
 — see Hibbert.
 — see Raff.
- TOMLINSON, J., see Gustavson.
- TOOVEY, T. W., Two-stage hypochlorite bleaching, 521, 529.
 — see Schmidt.
- see Sprout.
- TOTH, G., see Grassmann.
- see Zechmeister.
- TOWER, G. E., see Dean.
- TRAYNARD, P., see Guillemonat.
- TREER, R., see Kratky.
- TREIBS, W., see Fischer.
- TRENDELENBURG, R., Hard fibers, 18.
 — Specific gravity of wood, 29.
 — Structure of wood fiber, 358, 390.
- TROBECK, K. G., see Bergström.
- TROGUS, C., see Hess.
- TROMP DE HAAS, R. W., see Tollens.
- TROPSCH, H., and PHILLIPPOVICH, A. V., Heating of cellulose with water, 104.
- TROPSCH, H., see Fischer.
- TRYGG, L. H., see Hägglund.
- TSCHIRCH, A., and STOCK, E., Resin in wood, 332, 337, 387.
- TUOMINEN, M., see Hägglund.
- TURNER, H. D., see Plow.
- TYDÉN, H., Fractionation of cellulose, 85, 170.
 — α -Cellulose, 453, 471.
 — see Kullgren.

U

- UEBEL, O., see Ender.
- ULFSPARRE, S., Evaporation of sulfite waste liquor, 429, 464, 468.
 — see Brunen.
- ULMANN, M., see Hess.
- UMEZU, M., see Hachihama.
- UNGAR, E., Color reactions of wood, 185, 186, 188, 191, 193.
 — Addition of HCl to lignin, 214, 372.
 — Acid lignin, 263, 264, 267.
 — Determination of lignin, 267.
 — Veratric acid from methylated wood, 311.
- UNGER, E., and JÄGER, R., Condensation of aldehydes with barbituric acid, 188, 369.
- UNKAUF, H., see Peterson.
- see Wise.
- UNRUH, C. C., and KENYON, W. O., Oxidation of cellulose with nitrogen tetroxide, 83, 169.
- UNRUH, C. C., MCGEE, P. A., FOWLER, W. F., JR., and KENYON, W. O., Oxidation of cellulose with nitrogen tetroxide, 83, 169.
- UNRUH, C. C., see McGee.
- URBAN, H., Alkali lignin, 258.
 — Thermal decomposition of different lignin preparations, 268, 379.
 — Methylation of lignin, 285, 299, 381.
 — Methylation of wood, lignin, and cellulose, 299.
 — Determination of lignin, 329.
 — see Hägglund.

V

- VAINS, A. R. DE, Chlorine alkali pulping, 502, 505.
- VALKO, E., Structure of the cellulose molecule, 50, 164.
- VANZETTI, B. L., Formation of lignin, 321.
- VANZETTI, B. L., and DREYFUSS, P., Olivil, 322, 340, 385, 388.
- VAUHKONEN, T., see Routala.
- VAUPEL, O., see Schulze.
- VELDHUIS, M. K., Enzymatic degradation of cellulose, 115.
- VENN, H. J. P., Distillation of cellulose, 102, 172.
- VERMAAS, D., see Hermans.
- VESTERBERG, K. A., Dehydrogenation of abietic acids, 338.
- VIALARD, R., see Champetier.
- VILLIGER, V., see Baeyer.
- VINCENT, G. P., Sodium chlorite in bleaching, 521, 529.
- Bleaching with a mixture of chlorine and chlorine dioxide, 523, 530.
- VINCENT, G. P., RUSSEL, L. E., and WOODSIDE, K., Activation of chlorites with hypochlorite, 523, 530.
- VINCENT, G. P., see Brennan.
- see Taylor.
- see White.
- VINCENT, O., see Hägglund.
- VIOLETTE, H., Wood carbonization, 531, 539.
- VIRTANEN, A. I., Localization of cellulose in the cell wall of bacteria, 114, 115.
- Formation of acetic acid in thermophilic cellulose fermentation, 115.
- Chemical combination of lignin and cellulose, 304.
- VIRTANEN, A. I., and HUKKI, F., Action of cellulose fermenting bacteria upon wood and wood pulps, 115, 173.
- VIRTANEN, A. I., and KOISTINEN, O., Enzymatic degradation of wood and wood pulp, 303.
- VIRTANEN, A. I., KOISTINEN, O., and KIURU, V., Enzymatic degradation of wood and wood pulp, 115, 173, 303.
- VIRTANEN, A. I., and NIKKILÄ, O. E., Enzymatic degradation of wood and wood pulp, 115, 173, 303, 384.
- VITUCCI, J. C., see Nord.
- VOERKELIUS, G. A., Wood saccharification with dilute acids, 394.
- Wood saccharification with concentrated sulfuric acid, 400.
- VOGEL, H., Sulfite waste liquor (monograph), 467.
- VOIGTMAN, E. H., see Kress.

- VOSS, W., BAUER, R., and PFIRSCHKE, J., Arabinose in xylan preparations, 138, 176.
- Ratio between xylan and cellulose, 141.
- VOSS, W., BAUER, R., PFIRSCHKE, J., and BUTTER, G., Fractionation of xylan, 139, 176.
- VOTOČEK, E., and POTMĚŠIL, R., Determination of lignin, 332, 387.

W

- WACEK, A. v., Model substances for lignosulfonic acid, 232.
- WACEK, A. v., and DÄUBNER-RETTENBACHER, H., Oxidative degradation of phenol lignin, 247.
- WACEK, A. v., and DAVID, E., Model experiments on vanillin formation, 232, 374.
- WACEK, A. v., and KRATZL, K., Nitrobenzene oxidation of lignosulfonic acid models, 232, 234, 375.
- Formation of acetaldehyde from lignosulfonic acid, 233, 375.
- WACEK, A. v., KRATZL, K., and BÉZARD, A. v., Model substances for lignosulfonic acid, 232, 374.
- WACEK, A. v., and NITTNER, E., Constituents of beech wood tar, 534.
- WÄLCHI, O., see Frey-Wyssling.
- WAENERLUND, L., see Hägglund.
- WAENTIG, P., Chlorine alkali pulping, 502, 505.
- Pomilio process, 502, 505.
- WAENTIG, P., and GIERISCH, W., Chlorine number, 214, 331.
- WAENTIG, P., and KERENYI, E., Chlorine number, 214, 331.
- WAGNER, K., see Rassow.
- WAGNER, K. H., see Scheunert.
- WAHLBERG, H. E., Extraction of wood with benzene, 336.
- Reddening of sulfite pulp 454.
- WAKSMAN, S. A., Humic acids, 553, 554, 562.
- WAKSMAN, S. A., and CORDON, T. C., Bonds between lignin and cellulose, 560.
- WAKSMAN, S. A., and PURVIS, E. R., Theory of humus formation, 554, 563.
- WAKSMAN, S. A., and SMITH, H. W., Demethylation of lignin by microorganisms, 559.
- WALCH, H., see Freudenberg.
- WALD, W. J., RITCHIE, P. F., and PURVES, C. B., Periodate lignin, 278, 283, 380.
- WALDE, A. W., Treatment of lignin with hypobromite and hypiodite, 272.

- WALKER, R. D., and MORGAN, R. A., *Torula* yeast from sulfite waste liquor, 463.
- WALLER, A., Cymene yield from sulfite cooking, 457, 472.
— see Hägglund.
- WALLIN, H., and ODÉN, S., Pressure heating of black liquor, 494.
— Pressure heating of wood with alkali, 544.
- WALTER, P., see Jonas.
- WAN CHEN, W.-H., and CAMERON, F. K., Bleaching with chlorine dioxide, 132, 175.
- WATT, C., and BURGESS, H., Pressure heating of wood with alkali, 414.
— Soda pulping, 474.
- WEBER, O. H., Carboxyl groups in cellulose, 46, 163.
— see Husemann.
- WEBER, R., Mineral constituents of wood, 349.
- WEBJÖRN, B., see Hägglund.
- WEDEKIND, E., Dioxane lignin, 244.
- WEDEKIND, E., and ENGEL, O., Pulping with dioxane, 129.
- WEDEKIND, E., ENGEL, O., STORCH, K., and TAUBER, I., Phenol lignin, 247, 377.
— Molecular size of lignosulfonic acid, 224, 373.
- WEDEKIND, E., and GARRE, G., Iodination of lignin, 214, 289, 372, 382.
- WEDEKIND, E., and KATZ, J. R., Molecular size of acetyl phenol lignins, 296.
- WEDEKIND, E., see Engel.
- WEDENEJEW, W., see Bujewskoi.
- WEGELIUS, T., Anatomic structure and pulping properties of wood, 24.
- WEHMER, C., White rot and red rot, 559.
- WEHRLI, W., see Karrer.
- WEIDENHAGEN, R., Cellulase and cellobiase, 45, 163.
- WEIDINGER, A., see Hermans.
- WEINREB, K., see Pringsheim.
- WEISS, J. J., Hypochlorite bleaching, 519.
- WEISSENBERG, K., see Polanyi.
- WELCH, L. M., ROSEVEARE, W. E., and MARK, H., Fibrils in rayon fibers, 69.
- WELLS, S. D., Effect of sulfur in soda pulping, 488, 496.
- WELLS, S. D., and EDWARDS, V. P., Nitrocellulose, 120, 174.
- WELLS, S. D., GRABON, R. H., STAIDL, J. A., and BRAY, M. W., Kinetics of soda pulping, 476, 495.
- WELLS, S. D., and SCHELBORN, F. B., Multistage sulfate bleaching, 521, 529.
— Decrease in viscosity during chlorination of pulp, 525, 529.
- WELLS, S. D., see Rue.
- WELTZIEN, W., and TOBEL, G. ZUM., Oxidation of cellulose in the presence of alkali, 82.
- WENZEL, F., Color reactions of wood, 185, 369.
- WENZL, H., Determination of lignin, 329.
— Chlorine alkali pulping, 502, 505.
— Sodium chlorite for bleaching, 503, 505.
— Chlorine dioxide bleaching, 526, 530.
- WERGIN, W., Formation of "elementary fibrils," 58.
— see Hess.
- WESSLÉN, G., see Bergström.
- WEST, C. J., Utilization of sulfite waste liquor (bibliography), 467.
— Bibliography of tall oil, 492.
- WEST, K. A., HAWKINS, W. L., and HIBBERT, H., Constitution of lignin, 308, 384.
- WEST, K. A., MACGREGOR, W. S., EVANS, T. H., and HIBBERT, H., Alcoholysis of wood, 241.
- WEST, K. A., see Patterson.
- WESTLIN, A., see Samuelson.
- WETTSTEIN, R., see Jayme.
- WEYGAND, C., see Franz.
- WHEELER, A. S., and HARRIS, C. R., Formation of borneol during sulfite cooking, 463.
- WHEELER, A. S., and SMITHEY, T. W., Purification of crude cymene, 457, 472.
- WHEELER, D. H., see Anderson.
- WHEELER, H. J., and TOLLENS, B., Wood gum, 138.
- WHISTLER, R. L., see Martin.
- WHITE, A. A., see Merritt.
- WHITE, A. H., Dry distillation of black liquor, 493, 497.
- WHITE, A. H., and RUE, J. D., Dry distillation of black liquor, 493.
- WHITE, E. V., Arabinose and galactose, 152.
- WHITE, E. V., SWARTZ, J. N., PENISTON, Q. P., SCHWARTZ, H., MCCARTHY, J. L., and HIBBERT, H., Chlorination of pulp, 510, 512, 514, 516, 528.
— Chlorination of lignin, 272, 380.
- WHITE, E. V., TAYLOR, M. C., and VINCENT, G. P., Chlorite bleaching, 522.
— Action of chlorite on aldehydes, 524.
— Acid chlorite bleaching, 524.

- WHITE, E. V., and VINCENT, G. P., Acid chlorite bleaching, 503, 505, 524, 530.
— Yellowing and chlorite bleaching, 527.
- WHITE, E. V., see Taylor.
- WHITTAKER, H., see Powell.
- WHITTEMORE, E. R., REID, J. D., and LYNCH, D. F. J., Analysis of waste liquor from nitric acid pulping, 504, 505.
- WICHELHAUS, H., Tar formation during wood distillation, 534, 539.
- WIDELL, T., Carbonization of wood, 538.
- WIDMER, F., see Karrer.
- WIECHERT, K., Color reactions of wood, 184, 188, 369.
— Determination of lignin, 328.
- WIENHAUS, H., Isomerization of native resin acids during sulfite pulping, 458.
- WIESNER, J. v., Color reactions of wood, 183, 368.
— Resins in wood, 332, 337, 387.
— Dermatosomes, 361.
- WILCOXSON, L. S., see Tomlinson.
- WILKENING, L., see Ost.
- WILEY, A. J., JOHNSON, M. J., MCCOY, E., and PETERSON, W. H., Fermentation of sulfite waste liquor, 464.
- WILLE, H., see Friese.
- WILLSTÄTTER, R., Determination of lignin, 329.
— Wood saccharification with concentrated hydrochloric acid, 402, 413.
- WILLSTÄTTER, R., and KALB, L., Reduction of lignin, 273.
- WILLSTÄTTER, R., and ZECHMEISTER, L., Hydrolysis of cellulose, 43.
— Hydrochloric acid lignin, 264, 266, 379.
— Wood saccharification with concentrated hydrochloric acid, 402.
- WILSON, J. A., and KERN, E. J., Tannin content of different woods, 345.
- WILSON, K., Determination of carboxyl groups in oxycellulose, 85.
- WILSON, W. J., see Haworth.
- WINOGRADSKY, S., Aerobic cellulose bacteria, 112.
- WINQUIST, N., Regeneration of black liquor alkali, 494, 497.
- WINSVOLD, A., see Heuser.
- WINTZELL, T., see Holmberg.
- WISE, L. E., Structure of cellulose, 121.
— Hemicelluloses and paper properties, 137.
— Chemistry of hemicelluloses, 137.
- WISE, L. E., and APPLING, J. W., Biochemical method for determination of polysaccharides, 153.
- WISE, L. E., HAMER, P. L., and PETERSON, F. C., Galactose and arabinose from *Larix occidentalis*, 151, 178.
- WISE, L. E., and MOORE, S. T., Sterol from black spruce, 339.
- WISE, L. E., MURPHY, M., and D'ADIECO, A. A., Holocellulose, 132, 175.
- WISE, L. E., and PETERSON, F. C., Galactose and arabinose from *Larix occidentalis*, 151, 178.
- WISE, L. E., PETERSON, F. C., and HARLOW, W. M., Delignification of spruce and birch wood with ethanolamine, 133.
- WISE, L. E., and RATCLIFF, E. K., Holocellulose, 132, 176.
- WISE, L. E., and RITTENHOUSE, R. C., Arabinose in pine and kraft pulp, 142.
- WISE, L. E., and RUSSELL, W. C., Cellobiase yield from wood cellulose, 118.
- WISE, L. E., and UNKAUF, H., Galactose and arabinose from *Larix occidentalis*, 151, 178.
- WISE, L. E., see Harlow.
— see Hawley.
— see Isenberg.
— see Peterson.
- WISLICENUS, H., Incrustation theory, 297.
- WISLICENUS, H., and BÜTTNER, G., Dry distillation of cellulose, 108.
- WISLICENUS, H., see Büttner.
- WITTENBERGER, K., see Kürschner.
- WÖHLER, P., see Kerp.
- WOHL, A., Recovery of hydrochloric acid from wood saccharification by dialysis, 408, 413.
- WOHL, A., and BLUMRICH, K., Reversion of glucose, 94.
- WOHL, A., and KRULL, H., Wood saccharification with hydrochloric acid, 409.
- WOLFROM, M. L., and GEORGES, L. W., Degradation of cellulose with concentrated hydrochloric acid, 100.
- WOLFROM, M. L., SOWDEN, J. C., and LASSETTRE, E. N., Degradation of trimethyl cellulose, 100, 171.
- WOLFROM, M. L., see Dickey.
- WOLKOFF, L., Selenium content of cooking liquor, 425, 468.
- WOOLLOXALL, J. L. D., see Briggs.
- WOODHOUSE, H., see Denham.
- WOODSIDE, V., see Vincent.
- WOODWARD, E. R., Commercial preparation of chlorine dioxide, 521, 529.
- WRIGHT, G. F., and HIBBERT, H., Formic acid lignin, 252.

- WRIGHT, G. F., see Bell.
 — see Bond.
 — see Hunter.
 WRIGHT, K. A., see Ritter.
 WULTSCH, F., Flour-like particles in pulp, 454.
 WUHRMANN, K., HEUBERGER, A., and MÜHLETHALER, K., Ultrasonic wave treatment of fibers, 57.
 WURSTER, C., Color reactions of wood, 183.
 WURZ, O., Pectin in sulfite pulp, 155.
 WURZ, O., and SWOBODA, O., "Flour"-content of pulp, 453.
 WYK, A. J. A. VAN DER, and MEYER, K. H., Structure model of cellulose, 54.
 WYK, A. J. A. VAN DER, and STUDER, M., Absence of carboxyl groups in cellulose, 46.

Y

- YACKEL, E. C., and KENYON, W. O., Calcium salts of celluronic acids, 49, 164.
 — see Kenyon.
 YAMAMOTO, G., see Keimatsu.
 YIRAK, J. J., see Brauns.
 YLI-JAMA, O., see Routala.
 YORSTON, F. H., Fractionation of alkali lignin, 257.
 — see Green.
 — see Maass.
 — see Potter.
 — see Rashback.
 YOSHIKI, Y., and ISHIGURO, T. J., Hino-kinin, 340, 388.
 YÜ-CHARNG HWANG, see Hess.

Z

- ZAK, H., Sulfite waste liquor as tanning agent, 465.

- ZART, A., D. P. and mechanical properties of rayon, 68.
 — Oxidation of cellulose in the presence of alkali, 82, 169.
 ZECHMEISTER, L., Hydrolysis of cellulose with hydrochloric acid, 98.
 — Reactions between amines and wood, 186.
 — Linkages between lignin and carbohydrates, 299, 383.
 ZECHMEISTER, L., and TÓTH, G., Acetolysis of cellotriase, 44.
 ZECHMEISTER, L., see Grassmann.
 see Willstätter.
 ZEH, L., see Heuser.
 ZEISEL, S., Tannins, 345, 389.
 ZEISEL, S., and STRITAR, M. J., Determination of cellulose, 126.
 ZELLSTOFF-FABRIK WALDHOF, and HOTTENROTH, V., Recovery of sulfuric acid from wood saccharification, 402, 413.
 — Wood saccharification, 410.
 ZEMPLÉN, G., Cellobiose, 42.
 ZETTERLUND, C. G., Wood saccharification with dilute acids, 391.
 ZETZSCHE, F., Colorimetric determination of lignin, 184, 368.
 — Humic acids, 556, 563.
 ZETZSCHE, W., see Schaarschmidt.
 ZICKMANN, P., see Rassow.
 ZHIFLE, H. M., see Philipp.
 ZIMMERMANN, H., Ash content of different layers of the trunk of red beech, 347.
 ZOCHER, H., see Berkman.
 — see Freudenberg.
 — see Saechtling.
 ZSCHENDERLEIN, A., see Rassow.
 ZSIGMONDY, R., Crystal structure of textile fibers, 50, 164.
 ZYÓDAI, S., see Hachihama.

SUBJECT INDEX

A

Abietic acid, 338
 Acetaldehyde, liberation from lignosulfonic acid, 190, 233
 Acetic acid
 alkali lignin degradation, formation in, 258
 alkaline pressure heating of lignin, formation in, 269
 alkaline pressure heating of wood, yield from, 543, 544
 black liquor, preparation from, 494
 caustic fusion of lignosulfonic acid, formation in, 227
 caustic fusion of wood, formation in, 542
 cellulose fermentation product, 111, 113
 cuproxam lignin, formation from, 276
 dry distillation of cellulose, formation in, 108
 dry distillation of lignin, formation in, 267, 350
 sulfate process, formation in, 494
 sulfite process, formation in, 456
 wood distillation product, 531-538
 wood hydrolysis, formation in, 105
 wood saccharification, formation in, 394
 wood, yields from, 351, 353-356
 Acetic acid lignin, 247-252, 284
 Acetoguaiacone
 from lignosulfonic acid, 231, 467
 sulfate process, formation in, 488
 Acetone
 alkaline pressure heating of wood, formation in, 543, 544
 black liquor, preparation from, 493, 494
 butanol lignin, formation from, 240
 dry distillation of cellulose, formation in, 108
 dry distillation of lignin, formation in, 267
 wood distillation product, 532-536
 wood saccharification, formation in, 395, 399
 Acetosyringone, 231
 Acetovanillone (see Acetoguaiacone)
 Acetylbenzylcarbinol, 202
 Acetyl groups, presence in wood, 349, 356-357
 Adipic acid, 228
 Agathidicarboxylic acid, 338
 Alcohols (see names of individual alcohols)

Alcohol lignin, 237-246
 Alcoholysis of wood, 237-246
 Aldonic acids, 433
 Alkali celluloses, 77
 Alkali lignin, 255-261
 Alkaloids, 347
 Allyl alcohol, from butanol lignin, 240
 Amines
 lignin, isolation of, 254-255
 lignin, reagents for, 183 ff.
 lignosulfonic acid, precipitation of, 219 ff.
 Ammonia, use in sulfite cooking liquor, 435
 Amorphous and crystalline regions in cellulose, 56-62
 Amyrin, 338
 "Aniline wood," 560
 Anisic acid, from straw lignin, 258
 Annual rings, 1, 14, 28
 Anthocyanidins, 346
 Anthocyanins, 346
 Araban, 142-144
 Arabinose, 138, 142
 Arabogalactan, 152
 Ash, content and composition in wood, 17, 37, 351-354
 Aspen
 D. P. of cellulose from, 124
 lignosulfonic acid from, 198, 223
 native lignin from, 195
 pressure hydrogenation of methanol lignin from, 245
 Asplund process, 105
 Auxins, 13

B

Bacteria
 cellulose, action on, 109-116
 wood, action on, 109-116
 Bacterial cellulose, 58
 Balsams, 333 ff.
 Barbituric acid, use in furfural precipitation, 143
 Barium lignosulfonate (see also Lignosulfonic acid), 198, 219
 Bark, 17, 358
 Bast, 12
 Beech
 alkaline pressure heating of, 544
 lignin content, 325
 nitric acid pulping, 504
 sulfite pulp, maximum strength of, 452
 Benzoin, 202
 9,10-Benzophenanthrene, 273

- Benzyl alcohol groups
 lignin, presence in, 203
 methylation, 288
 sulfonation, 203
- Benzyl alcohol lignin, 241
- Benzyl ethers
 sulfonation, 203
 transetherification, 288
- Berberine, 347
- Betulin, 338
- Birch
 alkaline pressure heating, 543
 dry distillation, 532
 sulfite pulping, 448
- Bis(*p*-dimethylaminophenyl)methane,
 221, 222, 285
- Black liquor
 alkali recovery, 492-493
 constituents, 475, 481
 pressure heating, 494
 Rinman process, 493
 sulfate soap from, 491
- Bleaching
 alkali washing, 516-518
 bleach demand, 513
 buffered bleaching, 520
 chlorination, 508-516
 effect of pH, 511
 kinetics, 509
 lignin removal by, 510
 mechanism of, 513
 sulfate pulp, 510, 527
 chlorine dioxide and chlorites, 521-524
 chlorite, activation of, 522
 chlorolignin
 kinetics of dissolution, 511
 solubility of, 510
 hypochlorite, 518-521
 oxidation of cellulose, 519
 pulp brightness, permanence of, 526
 pulp characteristics, influence on, 524-527
 semichemical pulp, 501
- Borneol, 334, 462, 463
- Brazilin, 345
- Bromolignin, 280
- α -Bromomethylfurfural, 102
- 5-Bromovanillin, 280
- 6-Bromovanillin, 280
- Brown rot fungus, 561
- Brucine, 347
- "Burnt cook," 236, 423, 424
- Butanol lignin, 238-240
- Butanone
 black liquor, preparation from, 493
 alkaline pressure heating of wood,
 formation in, 544
- Butyl alcohol
 by fermentation of sulfite waste
 liquor, 463, 464
 wood saccharification, formation in,
 399
- 2,3-Butylene glycol, formation in wood
 saccharification, 399
- Butyraldehyde, formation from butanol
 lignin, 240
- Butyric acid
 cellulose fermentation product, 111,
 113
 alkali degradation of lignin, forma-
 tion in, 279
 caustic fusion of lignin, formation
 in, 269
 fermentation of sulfite waste liquor,
 formation in, 464
- C
- Cadinene, 334
- L-Cadinol, 334
- Calcium hypochlorite, bleaching with, 521
- Calcium lignosulfonate (see also Ligno-
 sulfonic acid), 235, 464
- Calcium sulfate, formation in sulfite
 process, 426-429
- Cambium, 1, 12, 17
- L-Camphene, 334
- Carbon dioxide
 bleaching, formation in, 520
 dry distillation of cellulose, forma-
 tion in, 108
 sulfite process, formation in, 457
- Carbohydrates (see names of individual
 sugars etc.)
- Carbonization of wood, 531-538
- Carbon monoxide, formation in dry dis-
 tillation of cellulose, 108
- Carbonyl groups, presence in lignin, 287
- Carboxyl groups
 in cellulose, 46
 in lignin, lack of, 287
 in lignosulfonic acid, 225
- Carene, 492
- Cataldi process, 502
- Catechin, 345
- Cell cavity (see Lumen)
- Cell wall
 dimensions, 23
 structure of, 358-366
- Cellobiase, 45
- Cellobiose
 from cellobiose octaacetate, 42
 in spruce cellulose, 119
 molecule, dimensions, 45
 octamethyl derivative, 44
- Cellobiose octaacetate, 42, 118
- Cellohexaose, 44
- Cellopentaose, 44

- Cellophane, action of microorganisms, 115
Cellotetraose, 44
Cellotriose, 44
 hendecamethyl derivative, 44
Cellulase, 45
Cellulosans, 135-136
Cellulose (see also Alkali celluloses, Cellulosans, Cotton, Holocellulose, Hydrate cellulose, Hydrocellulose, Oxycellulose)
 accessible regions, 50-62
 acetolysis, 42-45
 addition compounds with sulfuric and phosphoric acids, 86-87
 aldehyde end groups, 45
 alkalies, degradation by, 102-103
 α -cellulose, 121, 131, 353-354, 453
 amorphous and crystalline regions, 56-62
 destruction of crystalline structure by grinding; recrystallization, 62
 determination by chemical methods, 59-61
 determination by physical methods, 56-59
 recrystallization during hydrolysis, 61
 anisotropy, 44
 bacteria, action of, 109-116
 benzene, pressure heating with, 109
 β -cellulose, 353-354
 carboxyl groups in, 46
 caustic fusion, 103
 cellulosans, association with, 135-136
 chemical reactivity in the solid phase, 58
 chlorine dioxide and chlorite, action of, 521-524
 coalification, 104
 color reaction, 38
 content in different woods, 350-358
 copper number, 84
 cotton and wood, comparison of, 118-124
 cross-linking, 48-49
 Cross and Bevan determination, 125
 cuprammonium solutions, optical rotations of, 121
 definition, 40-42, 121
 degradation by dry hydrogen bromide, 102
 degradation by dry hydrogen chloride, 101
 degradation by hydrofluoric acid, 101
 degradation by mineral acids, 97-102
 degree of polymerization, 67-76
 density, 59
 determination, 124-134
 bromine-ammonia method, 126
 chlorination method, 125
 chlorine dioxide method, 132
 Cross and Bevan method, 125
 dioxane method, 129
 ethanolamine method, 133
 Hägglund method, 129-131
 Klason method, 127
 phenol for, 129
 resistant pure cellulose, according to G. Jayme, 133
 deuterium, reaction with, 60
 diffusion studies, 70-72
 dissociation constants, 46
 dissolved cellulose, micelles or molecules, 63-66
 dry distillation, 106-109
 electron microscopy, 57, 91
 elementary cell, 50-56
 end groups, determination of, 45-48
 enzymatic degradation, 45, 109-116
 fiber strength, 56, 116-118
 fungi, action of, 112-113, 558-562
 γ -cellulose, 353-354
 β -glucosidic linkages, 45
 hemiacetal linkages, 79
 humus, relation to, 553-562
 hypochlorite bleaching, oxidation in, 518-521
 insolubility in water, 54
 interfibrillar substance, 79
 kinetics of mild hydrolytic decomposition, 87-88
 kinetics of saccharification, 92-97
 linkages with lignin, 206, 297, 301-305
 macroheterogeneous reactions, 63
 mercerization, 77
 methylation, 43, 122-123, 299
 micellar-heterogeneous reactions, 62
 moisture regain, 63
 natural decomposition, 553-562
 network-formation, 48
 nitrogen dioxide, effect of, 49
 oxidation (see Oxycellulose)
 periodic acid, action of, 83
 permutoid reactions, 63
 polymolecularity, 68-69
 pressure hydrogenation, 274-276
 shape of cellulose molecules in solution, 75-76
 skin substance, 79
 specific gravity, 29
 sulfolysis, 86-88
 surface reactions, 63
 swelling in alkali, 77
 thallium ethylate, reaction with, 66
 ultracentrifuge studies, 70-75
 vacuum distillation, 102, 106-107
 viscosity of solutions, 67-68
 water, pressure heating with, 103-104

- weak linkages, 89-91
 - X-ray investigations, 49 ff., 121
 - Cellulose acetate, molecular weight by light scattering method, 75
 - Cellulose derivatives
 - analogous polymeric series, 66
 - degree of polymerization, 66-76
 - state of solutions, 65-66
 - Cellulose micelles
 - crystalline and amorphous regions, 55-57
 - dimensions, 55
 - electron microscopy, 91
 - fringe micelles, 57, 64
 - intermicellar spaces, 54-56
 - Cellulose nitrate, degree of polymerization, 124
 - Cellulose phthalate, 49
 - Cellulose xanthate
 - state of solution, 64
 - theory of micellar reactions, 64
 - Celluronic acids, 17, 83
 - insoluble calcium salts of, 49
 - Chalcones
 - sulfonation, 200
 - ultraviolet absorption, 318
 - Charcoal formation (see Wood distillation)
 - Chemigroundwood process, 500
 - Chestnut gallic acid, 345
 - Chloral lignin, 244
 - Chlorine
 - bleaching, effect of pH, 511
 - reaction with lignin, 510
 - Chlorine water, chemistry of, 507
 - Chlorine dioxide
 - bleaching with, 521-524
 - cellulose determination, use in, 132
 - Chlorine number, 214, 331
 - Chlorites, bleaching with, 521-524
 - Chlorolignin, formation in bleaching, 510
 - 5-Chlorosalicylic acid, 247
 - Chrysin, 346
 - Cinnamaldehyde, 187
 - Cinnamyl alcohol, formaldehyde from, 291
 - Clostridium butylicum*, fermentation of sulfite waste liquor, 464
 - Coal
 - cellulose, relation to, 553-557
 - lignin, relation to, 553-557
 - Cerulignol (see Dihydroeugenol)
 - Combes reaction, 192
 - Compound middle lamella, 17
 - Compression wood, 24-26
 - chemical composition, 357
 - Conidendrin, 322, 340-342
 - Coniferaldehyde
 - acid treatment, 265
 - aromatic amines, color reactions with, 187-189
 - bisulfite compound, 190
 - color reactions, 183, 187-189
 - decomposition by dilute alkali, 190
 - isolation from hadromal, 184
 - Coniferaldehyde groups
 - in lignin, 189-190, 287
 - in lignosulfonic acid, 189-190
 - in wood 189-190, 288
 - Coniferin, 320
 - Coniferin oxide, acid treatment of, 265
 - Coniferyl alcohol, 187, 319
 - mushroom oxidase, action of, 323
 - Copper number
 - cellulose, 84
 - lignosulfonic acid, 222
 - Cotton (see also Cellulose)
 - adsorption capacity for gases, 55
 - cellobiose octaacetate, yield from, 118
 - degree of polymerization, 117
 - density, 59
 - fibers, internal surface of, 55
 - Coumarone, wood distillation product, 534
 - p*-Cresol, 282
 - m*-Cresol, formation from butanol lignin, 240
 - 2,5-Cresotic acid, from phenol lignin, 247
 - Cross and Bevan cellulose method, 125
 - Cuproxam lignin, 276-279
 - Cyanomacurin, 346
 - p*-Cymene
 - sulfite process, formation in, 457-458
 - wood saccharification, formation in, 395
- D
- Degree of polymerization of cellulose, 67 ff.
 - after beating, 117
 - α -cellulose, 453
 - in cotton and wood, 123
 - in nitrated wood cellulose, 124
 - number average, 73
 - osmotic pressure method, 70
 - ultracentrifugal methods, 70-74
 - sedimentation velocity, 71
 - sedimentation equilibrium, 71
 - viscosity method, 67-69
 - weight average, 73
 - Dehydroabietic acid, 338
 - Dehydrodiisoeugenol, 313
 - sulfonation, 199
 - Dehydrodiveratric acid, 279, 313
 - De Vains process, 502
 - Dextropimaric acid, 337
 - Dicotyledons, 1
 - Diethylene glycol, from methanol lignin, 246
 - Diffusion studies, 70-72
 - Diffuse porous wood, 2, 11
 - Dihydroabietic acid, 338

Dihydroeugenol, 258, 281
Dihydroxyphenylacetylcarbinol, 308
Dihydroxyphenylglycerol, 308
Dihydroxyphenylhydroxypropionaldehyde, 308
Dihydrositosterol, 339
22,23-Dihydrostigmaterol, 339
3,5-Dihydroxystilbene (see Pinosylvins)
3,3'-Dimethoxy-4,4'-dihydroxystilbene, 235
3,4-Dimethoxytoluene-*m*-sulfonic acid, 203
3,5-Dinitro-4-hydroxybenzaldehyde, 270
Dioxane lignin, 244, 285
Dipentene, 333, 457
Diphenylcarbinol, 202
Diveratrylether, 203
Dyes, occurrence in wood, 345-346

E

Early wood, 1
Egonol, 313
Ellagic acid, 345
Enzymatic degradation
 cellulose, 109-116
 lignin, 558
 wood, 109-116, 558
Epicatechin, 345
D-Erythrose, formation in cellulose oxidation, 83
Ethanol lignin, 237-246, 284
Ethanolysis of wood, 237-246
 α -Ethoxypropionguaiacone
 acid treatment of, 263
 ethanolysis product, 241
 hydrogenation of, 245
 α -Ethoxypropiosyringone, 241
Ethyl alcohol
 cellulose fermentation, formation in, 111, 113
 from sulfite waste liquor, 458-463
 from wood hydrolyzates, 392-399
o-Ethylanisole, 282
4-Ethylcyclohexanol, 246
Ethylene glycol, from methanol lignin, 246
 β -Ethyl- α -methylacrolein, from butanol lignin, 240
Eudesmin, 341
Eugenol, 188, 268

F

Fats, presence in wood, 332-335, 350-351
Fatty acids, presence in wood, 335
Fatty trees, 334
Ferruginol, 338
Ferulic acid, 187

Fibers
 dimensions, 20-24
 effect on pulp properties, 438
 libriform, 4
 morphology, 20-24
 strength, 116-118
Fiber wall, structure of, 358-366
Fibrils
 breakdown of rayon filaments, 69
 dimensions, 359-363
 formation
 by ultrasonic wave treatment, 57
 by wet-beating, 57
Fisetin, 346
Flavanones
 in *Pinus* species, 346
 sulfonation, 200, 318
 ultraviolet absorption, 318
Flavones in *Pinus* species, 346
Fodder yeast, from sulfite waste liquor, 463
Formaldehyde
 bisulfite addition compound in sulfite waste liquor, 429, 430
 dry distillation of cellulose, formation in, 108
 lignin and lignosulfonic acid, formation from, 290-292
 lignin models, formation from, 290 ff.
 wood distillation product, 532
Formic acid
 alkaline pressure heating of wood, formation in, 543-544
 alkaline pressure heating of lignin, formation in, 269
 caustic fusion of wood, formation in, 542
 cellulose fermentation product, 111, 113
 sulfite process, formation in, 456
 wood distillation product, 532-533
 wood hydrolysis, formation in, 105, 350, 356
Formic acid lignin, 247-252, 284
Fructan, 153, 356, 357
Fructosan (see Fructan)
Fructose
 determination of, 131
 Rheinau process, yield in, 407
Fungi
 cellulose, action on, 112-113, 558-564
 lignin, action on, 558-564
 wood, action on, 558-564
Furfural
 bisulfite addition compound in sulfite waste liquor, 429, 430
 determination, 143
 dry distillation of cellulose, formation in, 108

- wood distillation product, 535
 - wood saccharification, formation in, 395, 400
 - Furfuroids, 161
 - Fusel oil, 462
- G
- Galactan
 - determination, 151-152
 - wood, content of, 356-357
 - Galactose, 39
 - determination, 131
 - fermentation, 393
 - Rheinau process, yield in, 407
 - Gallic acid
 - from beech lignin, 279
 - in tannins, 345
 - Glucan, 148-151, 356, 357
 - Glucose
 - Rheinau process, yield in, 407
 - sulfocarboxylic acids, 434
 - Glucosyl chloride, 101
 - Glucosyl fluoride, 101
 - Glycerol lignin, 243
 - Glycolaldehyde, sulfonation of, 205
 - Glycol lignin, 243, 285
 - Glycolignose, 39
 - Glyoxal, formation in cellulose oxidation, 83
 - Gmelinol, 341
 - Guaiacol
 - from alkali lignin, 258
 - from hydrochloric acid lignin, 282
 - from lignosulfonic acid, 235
 - nitrobenzene oxidation of wood, 214, 280, 310
 - Guaiaretic acid, 339
- H
- Hadromal, 183-184
 - from fungus attacked wood, 560
 - Hägglund lignin determination, 326
 - Heartwood
 - age of tree and formation of, 15
 - extractives in, 15, 348
 - spruce, sulfite pulping of, 548
 - Helicin, 186
 - Helix pomatia*, cellulose-hydrolyzing enzymes from, 45, 110, 303
 - Hematoxylin, 346
 - Hemicellulose (see also Cellulosans, Mannan, Pentosans, Polyuronic acids, Nylans)
 - classification, 134-137
 - definition, 39
 - determination in wood, 130-132
 - wood, content of, 350-358
 - Hendecamethylcellotriose, 44
 - n*-Heptane, from wood turpentine, 334
 - Hexosans (see also Fructan, Galactan, Glucan, Mannan)
 - classification, 134-137
 - wood, content of, 350-358
 - Hinokinin, 340
 - Holocellulose
 - preparation, 131-133
 - sulfite cooking, 434
 - Homoveratrol, 281
 - Howard process, 465
 - Humal acids, 553
 - Humic acids, 104, 553-564
 - Humins, 553-564
 - Humus
 - cellulose, relation to, 553 ff.
 - formation, 553 ff.
 - lignin, relation to, 553 ff.
 - X-ray investigations, 554, 559
 - Hydrate cellulose
 - conversion into native cellulose, 78
 - filaments, 65
 - formation, 81
 - stretching and crystallinity, 65
 - X-ray investigations, 77
 - Hydrazine lignin, 254-255
 - Hydrocellulose, 78-81
 - aldehyde end groups, 81
 - chain length, 81
 - chain length and strength properties, 81
 - electron microscopy, 90
 - formation, 78
 - solubility in alkali, 78
 - X-ray diffraction, 79
 - Hydrochloric acid lignin (see Lignin), 264-276
 - Hydrogen sulfide, occurrence in sulfite waste liquor, 426
 - Hydrogen sulfide lignin, 483-484
 - Hydrol lignin, 262-263, 282
 - p*-Hydroxybenzaldehyde from straw lignins, 215
 - p*-Hydroxybenzoic acid, formation from glycol lignin, 243
 - β -Hydroxyconiferyl alcohol
 - "lignin progenitor," 315
 - rearrangement of, 315-316
 - 3-(4-Hydroxycyclohexyl)-1-propanol, 245, 281
 - 1-(4-Hydroxy-3,5-dimethoxyphenyl)-1-propanone, ultraviolet absorption, 292
 - 5-Hydroxymercurivanillin, 235
 - p*-Hydroxymesityl alcohol, 291
 - 1-(4-Hydroxy-3-methoxyphenyl)-1-propanone, ultraviolet absorption, 292
 - Hydroxymethylfurfural
 - determination of pentosan, formation in, 143
 - dry distillation of cellulose, formation in, 108, 120

α -Hydroxypropioquiainone, 202, 205, 241, 343
 hydrazine compound, 255
 α -Hydroxypropiosyringone, 323
 β -Hydroxypropioveratrone, 291
 Hymatomelanin acid, 104
 Hypochlorite, mechanism of bleaching, 518-521

I

Incrustation theory, 38, 181, 297
 Inter cellular passages, 8
 Iodolignin, 281
 5-Iodovanillin, 281
 Isodextropimaric acid, 337
 Isoeugenol, 282
 Isohemipinic acid, formation in lignin degradation, 277, 279, 206, 310-314
 Isolariciresinol, 312, 341
 Isoolivil, 312, 322, 341

K

Kalb lignin determination, 329
 Keebra process, 498
 Klason cellulose definition, 121, 127
 Klason cellulose method, 127
 Klason lignin determination, 324
 Knecht's compound, 77
 Kraft pulp (see Sulfate pulp)
 König and Rump lignin determination, 329
 Kürschner and Wittenberger lignin determination, 331

L

Lactic acid
 cellulose fermentation, formation in, 111, 113
 sulfite waste liquor fermentation, formation in, 461
 Lapachol, 346
 Lariciresinol, 312, 313, 341
 Late wood, 1
 Leucoanthocyanins, 346
 Levoglucosan, from cellulose, 102
 Levopimaric acid, 337-338
 Light scattering, 75
 Lignans, 322, 339-343
 Lignification, 306-324, 359
 Lignin (see also Lignosulfonic acid)
 acetal linkages, 195, 238-240
 acetic acid, isolation with, 247-252
 alcohols, isolation with, 237-247
 aldehyde groups, 201, 287
 alkaline degradation, 279
 alkali lignin, 255-261
 acetylation, 257
 chlorination, 260
 elementary composition, 256-257, 285

equivalent and molecular weights, 257, 489
 ethers from, 260
 ion exchangers from, 261, 466
 methylation, 257
 nitration, 260
 pressure hydrogenation, 259
 utilization, 260-261
 water soluble, 487

amines, color reactions with, 184 ff.
 amines, isolation with, 254-255
 analyses, 284-285
 aromatic character, 293
 benzyl alcohol, isolation with, 241
 benzyl alcohol groups in, 209, 313
 benzyl alkyl ether groups in, 209, 288
 biosynthesis, 306 ff.
 bromine, action of, 199, 272
 brown rot, action of, 561
 butanol lignin, 238-240
 acid degradation, 240
 electrolytic oxidation, 240
 butyl alcohol, isolation with, 238-240
 carbonyl groups in, 287-288
 carboxyl groups, lack of, 287
 catalytic pressure hydrogenation, 307
 caustic fusion, 227, 258, 279
 chloral hydrate, isolation with, 244
 chlorinated, removal in bleaching, 510
 chlorination, kinetics of, 511
 chlorine number, 214
 chlorine, treatment with, 214, 289
 color reactions, 181-193
 Combes color reaction, 192
 coniferaldehyde groups, presence of, 189-190, 287
 coniferyl alcohol, relation to, 320, 323
 constitution, 306-324
 cuproxam lignin, 276-290
 elementary composition, 284
 oxygen distribution in, 286
 potassium in liquid ammonia, treatment with, 302
 cyclic acetal groups, 201, 208, 315
 degradation, 279-282
 destructive distillation, 282
 determination of (see Lignin determination)
 dichroism, 304
 dioxane, isolation with, 196, 244, 297
 distribution in wood 297-306
 double bonds, 198-199, 289
 dry distillation, 267
 elementary composition, 282-290
 enzymatic degradation, 303-304
 ethanolamine, isolation with, 254
 formaldehyde, formation of, 290-292
 formed and unformed, 306

- formic acid, isolation with, 247-252, 284
- Freudenberg formulas, 250
- functional groups, 282-290
- glycerol, isolation with, 243
- glycerol monochlorohydrin, isolation with, 243
- glycol, isolation with, 243
- glycol chlorohydrin, isolation with, 243-244
- groups "A" and "B", 207 ff.
- "hadromal," relation to, 183-184
- Hibbert formulas, 317
- humic acid, relation to, 553 ff.
- humus, relation to, 553 ff.
- hydrazine, isolation with, 254-255
- hydrochloric acid lignin, 264-276
- alkaline pressure heating, 269
 - bromine, action of, 272
 - caustic fusion, 267, 269
 - diazomethane, methylation with, 311
 - dry distillation, 267-268
 - nitration, 270
 - oxidation, 270, 311
 - pressure hydrogenation, 274-275
 - reduction, 273
 - sulfonation, 266
- hydrogenation, 236, 244, 259, 274, 281-282
- hydrogen sulfide lignin, 483-484
- hydrol lignin, 262-263
- hydrotropic solutions, extraction with, 261-262
- β -hydroxyconiferyl alcohol, relation to, 315
- hydroxyl groups, 249, 251, 285-287
- incrustation theory, 38, 181, 297
- index of refraction, 294-295
- infrared absorption, 294
- iodine, treatment with, 289
- isolignan groups, 312
- lead tetraacetate, treatment with, 199, 289
- light absorption, 292-294
- lignan groups, 313
- α - and β -lignin, 219 ff.
- linkages with cellulose, 206, 297 ff.
- Mäule reaction, 193, 215
- maleic anhydride, treatment with, 289
- Masonite process, behavior in, 105
- methanol lignin, pressure hydrogenation, 244
- methoxyl content, 256, 284-287, 321, 325, 330-331
- methylation, 212, 299
- methylenedioxy groups, 290-292
- middle lamella, presence in, 293
- mineral acids, isolation with, 263 ff.
- model substances, sulfonation of, 200-212
- molecular weight, 295-297
- native, according to F. E. Brauns, 193 ff.
- aspen, isolation from, 195
 - carbonyl groups, presence of, 195
 - coniferaldehyde groups, presence of, 189, 288
 - organic solvents, extraction with, 193-196
 - phloroglucinol, color reaction with, 189
 - ultraviolet absorption, 195
- native, in the wood, 196
- alcohols, reaction with, 213
 - alkali sulfides, reaction with, 212-213
 - dichroism, 304
 - dioxane-hydrochloric acid, extraction with, 196
 - halogens, reaction with, 214
 - hydrogen halides, reaction with, 214
 - hydrogen sulfide, reaction with, 212-213
 - lignosulfonic acid from, 196-197, 415-422
 - mercaptans, reaction with, 213
 - methylation, 212
 - model substances, sulfonation of, 199-212
 - oxidation, 214-215
 - phenols, reaction with, 213
 - sulfite, reaction with, 196-212
 - ultraviolet absorption, 182, 292-294
- natural decomposition, 553-562
- oxidation
- degradation by, 280-281
 - with nitrobenzene 214-215
 - with ozone, 271
- oxygen rings, opening by sulfonation, 200
- periodate, isolation with, 278-279
- phenolic hydroxyl groups, 200, 204-205, 285-287, 302, 314
- phenols, color reactions with, 182 ff.
- phenols, isolation with, 246-247
- phloroglucinol, color reaction with, 183 ff.
- physical properties, 292-297
- polydispersity, 296
- primary carbinol groups, presence of, 313
- pressure hydrogenation, 259, 274-275
- red rot, action of, 558-561
- reduction, 273
- specific gravity, 31
- spectrochemistry, 182, 211, 292-294

Lignin (*continued*)

- sulfuric acid, isolation with, 263-264
- thioglycolic acid, isolation with, 252-254
- thiolignin (see Thiolignin)
- thiophenol, isolation with, 247
- ultraviolet absorption, 182, 211, 292-294
- ultraviolet microphotography, 293
- vacuum distillation, 268
- Wiesner reaction, 183 ff., 194
- white rot, action of, 558-559
- Willstätter lignin (see hydrochloric acid lignin)
- wood, content of, 17, 350-358

Lignin determination

- bromine uptake, 331
- chlorine number, 331
- colorimetric methods, 327
- Cross, Bevan, and Briggs method, 332
- dimethyl-*p*-phenylenediamine method, 185
- Hägglund method, 326
- hydrochloric acid method, 327-328
- hydrogen fluoride method, 328
- indirect methods, 329-332
- Kalb method, 329
- Klason method, 324
- Kürschner and Wittenberger method, 331
- König and Rump method, 329
- methods, comparison of, 329
- methoxyl content for, 330-331
- Noll method, 327
- phloroglucinol method, 332
- sulfuric acid method, 324-327
- Tingle number, 331

Lignin plastics, 260, 400, 466

Lignocellulose, 186, 400

Lignoceric acid, 335

Lignol, 257

Lignosans, 40

Lignosulfonic acid, 215-237, 414 ff.

- acetaldehyde, formation of, 190, 233
- acetoguaiacone from, 231, 467
- amines, precipitation with, 219 ff.
- from aspen, 198, 223
- bromination, 226
- carboxyl groups, 225
- caustic fusion, 228-237
- chlorination, 226
- color change during sulfite pulping, 434-436
- condensation during sulfite pulping, 423
- coniferaldehyde groups, presence of, 288
- copper number, 222-223
- dilute alkali, action of, 190
- dissolution, kinetics of, 216 ff.
- dissolved, properties of, 216-220

- elementary composition, 284-285
- esters, preparation of, 227
- fluorescence, 266
- formaldehyde formation of, 290-292
- free phenolic groups, 230
- halogens, treatment with, 226
- hydrogenation, 236
- ion exchanging properties, 216
- mannose, occurrence of, 223
- methoxyl content, 222, 224-226, 229
- methylation, 229
- molecular weight, 223-225, 295-297
- α - and β -naphthylamine, precipitation with, 219-222
- nitration, 227
- oxidation with nitrobenzene, 214
- phloroglucinol reaction, 189
- precipitation of, 219-225
- solid, formation of, 418
- spectrochemistry, 211, 292-294
- sulfonic acid groups, amount of, 225
- sulfur content of, 419 ff.
- surfen, precipitation with, 220
- tanning properties, 226
- thiocyanogen, treatment with, 227
- ultraviolet absorption, 211, 292-294
- vanillin, formation of, 229-235

α - and β -Lignosulfonic acids, 221 ff.

Lignosulfonic acid-carbohydrate compound, 301

D-Limonene, 334

L-Limonene, 334

Linoleic acid, 335

Linolenic acid, 335

Loosely bound sulfite, 189, 429-430

Lumen, 22

M

Maclurin, 346

Mäule reaction, 193, 215

Magnesium, use in sulfite cooking liquor, 437-438

Maleic acid, formation in alkali lignin oxidation, 258

Maltol, formation in dry distillation of cellulose, 108

Manganese, occurrence in wood ash, 349

Mannan

- determination in wood, 145-147

- viscosity of solutions, 68

- gymnosperms, content of, 147-148, 356-357

Mannose

- determination, 130

- lignosulfonic acid, occurrence in, 223

- Rheinau process, yield in, 407

Marsh humic acid, 104

Masonite process, 105

Matairesinol, 340

Meadol, 258, 260

Medullary rays, 2

- Melene, 268
- α -Mercaptoisobutyric acid lignin, 253, 284
- Mercapto lignins, 252-254, 284
- Metahemipinic acid, formation in lignin oxidation, 311-313
- Methanol lignin, 193 ff.
- Methoxyacetic acid, formation in lignin oxidation, 313
- 2-Methoxy-4-ethylcyclohexanol, 246
- Methoxyl groups
 in carbohydrates of spruce, 285
 in lignin 256, 284-287, 321, 325, 330-331
 in lignosulfonic acid, 222, 224-226, 229
 in wood, 17, 350, 355
- Mercerization, 77
- Methyl alcohol
 alkaline pressure heating of lignin, formation in, 269
 alkaline pressure heating of wood, formation in, 543-546
 black liquor, preparation from, 494
 from butanol lignin, 240
 caustic fusion of wood, formation in, 542
 dry distillation of cellulose, formation in, 108
 dry distillation of lignin, formation in, 267
 wood saccharification, formation in, 395
 sulfate process, formation in, 487, 491
 sulfite process, formation in, 457
 wood distillation product, 532, 533, 534, 536, 537
- Methylbenzoylcarbinol, 202
- Methylcellulose, distribution of substituents in, 63
- Methylenedioxy groups in lignin, 290-292
- Methylfurfural
 determination of pentosan, formation in, 143
 sulfite process, formation in, 457
- Methyl glyoxal, in sulfite waste liquor, 429, 430, 460
- 1-Methyl-7-isopropylphenanthrene (see Retene)
- Methyl mercaptan, formation in sulfate process, 487, 490
- Methyl-*p*-methoxycinnamate, 116
- Methylpentosans, 351-354
- Micelles (see also Cellulose micelles), 49 ff.
- Middle lamella, 17, 304-305
- Mineral constituents in wood, 347-349
- Mitscherlich test, use in sulfite pulping, 435
- Monocotyledons, 17
- Monohydroxyacetone, sulfonation of, 205
- Morin, 346
- N
- Neoabietic acid, 338
- Nitric acid pulp, 503-504
- Nitrocelluloses, molecular weights, 73-74
- Nitrogen in wood, 17, 347, 351
- 3-Nitro-4-hydroxybenzaldehyde, 270
- 3-Nitro-4-hydroxybenzoic acid, 270
- Noll lignin determination, 327
- Nonporous wood, 2
- Norconidendrin, 342
- O
- Oak, dry distillation, 536
- Octamethylcellobiose, 44
- Oleic acid, 335
- Oleoresins, 333
- Olivil, 340, 341
- Osmotic balance, 70
- Oxalic acid
 alkali lignin degradation, formation in, 258
 caustic fusion of cellulose, preparation by, 540-543
 caustic fusion of lignin, formation in, 269, 541
 caustic fusion of lignosulfonic acid, formation in, 228
 caustic fusion of wood, preparation by, 540-543
 cellulose fermentation product, 116
 cellulose oxidation product, 83
 nitric acid oxidation of carbohydrates, formation in, 543
- Oxycellulose, 81-86
 air oxidation, formation by, 82
 alkaline cleavage, 82, 84
 characteristic groups, determination of, 85
 dialdehyde type, alkalisensitivity of, 84
 furfural and carbon dioxide, formation of, 85
 nitrogen dioxide oxidation, formation by, 83
 periodate oxidation, formation by, 83
 permanganate oxidation, formation by, 83
- P
- Palmitic acid, 335
- Parenchyma, 4 ff.
 strands, 7
- Peat, 553 ff.
- Pectin, 153-155, 351, 357
- Peltogynol, 346
- Pentosans (see also individual sugars), 106 ff.
 determination in wood, 143
 wood, content of, 17, 350-357

- Periodate lignin, 278-279
 Permanganate number, use in sulfite pulping, 436
 1- β -Phellandrene, 334
 α -Phenethyl alcohol, 202
 α -Phenethyl thioglycolic acid, 203, 239
 Phenin, 346
 Phenizein, 346
 Phenol humic acids, 554
 Phenol lignins, 246-247
 Phenols
 influence on sulfite pulping, 244-248
 occurrence in wood, 343-347
 Phloem, 12
 Phloroglucinol,
 lignin, reagent for, 183 ff.
 color reaction, specificity of, 188
 Phytosterols, 339
 tall oil, occurring in, 492
 Pine
 dry distillation of, 536
 sulfite pulping, 443-448
 Pinene, 333, 334, 458, 492
 wood saccharification, formation in, 395
 Pinobanksin, 346
 Pinocembrin, 346
 Pinoresinol, 204, 341
 Pinostrobin, 346
 Pinosylvin, 15, 343, 344
 effect on sulfite pulping of pine, 445
 Pit, 4 ff.
 bordered, 5
 Pith, 8, 25-26
 Podophyllotoxin, 343
 Polymolecularity of cellulose, 68 ff.
 molecular weight, effect of, 74
 strength properties of rayon fibers, effect on, 68
 Polyoxymethylene, 67
 Polythionates, formation in sulfite process, 424
 Polyuronic acids, 41
 wood, content of, 356
 Pomilio process, 502
 Pores of wood, 2
 Porous wood, 2
 Potassium-liquid ammonia lignin, 285
 Prehydrolysis of wood
 followed by sulfate pulping, 489
 followed by sulfite pulping, 448
 Primary bark, 12
 Primary rays, 2
 Primary tar, formation in thermal decomposition of cellulose, 109
 Primary wall, 358
 Primary wood, 12
 Procambium, 12
 Propyl alcohol, formation from butanol lignin, 240
 1-Propyl-1,2-cyclohexanediol, 245, 281
 4-Propylcyclohexanol, 245, 246, 281
 Propylguaiacol, formation in alkali lignin distillation, 258
 Prosenchyma, 4 ff.
 Proteins, presence in wood, 17, 351, 356, 357
 Protocatechuic acid
 alkali lignin degradation, formation in, 258
 alkaline degradation of lignin, formation in, 279
 caustic fusion of hydrochloric acid lignin, formation in, 269
 caustic fusion of lignosulfonic acid, formation in, 227
 cuproxam lignin, formation from, 278
 Pulp (see also Semicheical pulp, Sulfate pulp, Sulfite pulp)
 bleached, post-color effect of, 526
 permanence of brightness, 526
 bleaching, strength losses during, 527
 degree of polymerization, 453
 properties, influence of wood character on, 438-443
 Pulping (see Semicheical pulping, Soda process, Sulfate process, Sulfite process)
 Pyrocatechol
 alkaline degradation of lignin, formation in, 279
 caustic fusion of lignin, formation in, 228, 269
 Pyroligneous acid
 composition of, 535
 tar elimination from, 535
 wood distillation product, 535
- Q
- Quebracho catechin, 345
 Quercetin, 345
 Quercitannic acid, 345
- R
- Rayon fibers
 D. P. and mechanical properties, 69
 fibrils, breakdown into, 69
 formaldehyde treatment, 49
 Rays, primary and secondary, 2
 uniseriate and multiseriate, 8
 Reaction wood, 24
 Reddening of unbleached sulfite pulp, 454-455
 Red rot fungi, 558-561
 Reductinic acid, 155
 Resenes, 337, 343
 Reserve celluloses, 39
 Resins, 332 ff.
 classification, 337
 extraction from wood, 335-337
 influence on sulfite pulping, 443-448
 wood, content of, 350-357

- Resin acids, 335, 337
Resin alcohols, 337
Resin ducts, 2, 8, 9
Resinotannin alcohols, 337
Resorcinol monomethylether, formation from butanol lignin, 240
 β -Resorcyclic acid, formation from butanol lignin, 240
Retene, 338
Rheinau process, 391, 404-408
Ring porous wood, 2, 11
Rinman process, 493
Roe chlorine number, 214, 331, 489
Roschier permanganate number, 436
Rosin, 338
- S
- Saccharification
 of cellulose, 92-102
 of wood, 390-413
Salicylic acid, from phenol lignin, 247
Santalol, 345
Scholler process, 336-337
Secondary rays, 2
Secondary wall, 359
Selenium, influence on stability of sulfite cooking liquor, 425
Semiacetal linkages in cellulose, 79, 90
Semichemical pulping, 498-505
Semi-Keebra process, 499
Sesquiterpenes, 334, 457
Sitosterol, 339
Skeletal celluloses, 39
Skeletal substance, 349
Skin substance, 64, 79, 364
Soda process
 components of black liquor, 475-476
 equivalent weight of dissolved lignin, 486
 kinetics, 476-477
 sulfur, use of, 488-489
Sodium hypochlorite, bleaching with, 518-521
Sodium chlorite, bleaching with, 521-524
Sodium sulfite, pulping with, 498-501
Sodium thiosulfate, use in alkaline pulping, 488
Specific gravity of wood, 29
Springwood, 1
 sulfite pulp properties, 438-443
Spruce
 alkaline pressure heating of, 543
 alkaline pulping of, 474 ff.
 growth conditions, effect on sulfite pulping, 438-443
Starch, 17, 102
Sterols, 339
Stigmasterol, 339
Stilben quinone, relation to sulfite pulp reddening, 454-455
Strychnine, 347
Succinic acid, 258
Sugar sulfonic acids, 223, 430-434
Sulfate process
 alkali recovery, 492-493
 by-products, 490-494
 demethylation of lignin, 487-488
 effect of wood prehydrolysis, 489
 effect of sulfidity, 477-487
 equivalent weight of dissolved lignin, 486
 hardwoods, use of, 490
 hydrogen sulfide lignin, 483-484
 hydroxyl ion concentration, 477
 kinetics of, 476-477
 lignin dissolution, mechanism of, 477-483
 molecular weight of dissolved lignin, 484
 pulp strength, influence of cooking time, 477-483
 pulp strength, influence of sulfidity, 477-483
 sulfate soap from, 491
 tall oil from, 491-492
 thiolignin, formation of, 482-487
 turpentine, yield of, 492
 volatile by-products, 490-492
Sulfate pulp
 bleaching of, 510, 527
 from prehydrolyzed wood, 489
 strength properties, 477-483
Sulfite charcoal, 236
Sulfite cooking liquor
 acidity, determination of, 419, 422-423
 effect of selenium, 425
 stability, 424-426
Sulfite process
 aldonic acids, formation of, 430-434
 ammonium bisulfite, use of, 437-438
 available sulfite, 434-436
 borneol, formation of, 462, 463
 "burnt cook," 423, 424
 by-products, 456-467
 carbon dioxide, formation of, 457
 color change of cooking liquor, 434-436
 cymene (sulfite turpentine), yield of, 457-458
 damaged chips, influence on pulp strength, 450
 cooking time, degree of pulping, determination, of 434-436
 dipentene, formation of, 457
 formic acid, yield of, 456
 formic acid, reaction with bisulfite, 433
 hydrolytic dissolution of lignosulfonic acid, 415-424
 hydrogen ion concentration, 415-424

T

- Sulfite process (*continued*)
 kinetics, 415-424
 magnesium bisulfite, use of, 437-438
 methyl alcohol, yield of, 457
 methylfurfural, formation of, 457
 pine, use of, 443-448
 polythionates and thiosulfate, formation of, 424
 sodium bisulfite, use of, 419, 437-438
 solid lignosulfonic acid, formation of, 418-419
 sugars, formation and destruction of, 430-431
 sugars, yield of, 430, 459
 sulfate, formation of, 426-429
 sulfocarboxylic acids from sugars, 434
 sulfonation and delignification, 415-424
 two-stage, for high alcohol yield, 459
 sulfur consumption, 418-419
 wood character, effect of, 438-443
- Sulfite pulp
 bleaching of, 506 ff., 527
 chemical composition, influence on strength properties, 449-454
 properties of, 449-456
 fluorescence of, 455-456
 reddening of, 454-456
 wood character, effect of, 438-443
- Sulfite turpentine (Cymene), 457, 458
- Sulfite waste liquor
 burning of, 461
 ethyl alcohol from, 458-462
 fermentation, 459 ff.
 fodder yeast from, 463-464
 Howard process, 465-466
 hydrogenation of, 467
 lignin plastics from, 466
 loosely bound sulfur dioxide, 456, 459-461
 sugars in, 463-464
 tanning properties of, 465
 use as fertilizer, 464
 vanillic acid from, 466-467
 vanillin from, 466-467
- Sulfite waste liquor lactone (Conidendrin), 322, 340-342
- Sulfuric acid lignin, 263-264
- Summerwood, 1
 sulfite pulping properties, 438-443
- Surfen, lignosulfonic acid precipitant, 220
- Sylvestrene, 333
- Syringaldehyde
 from different woody materials, 215
 from hardwood lignins, 280, 307
 from lignosulfonic acid, 231
- Syringoylmethyl ketone, 242
- Tall oil, 491-492
- Tannins, 17, 343, 347
- Tar, wood distillation product, 531-539
- Taxifolin, 15, 346, 447
- Tectochrysin, 346
- Tectoquinone, 345
- Tension wood, 24-26
- Terpenes, 333-334
 by-products in alkaline pulping, 492
 cymene, formation of, 457
 in "sulfite turpentine," 457
 wood saccharification, formation in, 395
- 1-Terpineol, 334
- Tetrahydroabietic acid, 338
- 2,3,5,6-Tetramethylgluconic acid, 44
- 2,3,4,6-Tetramethylglucose
 from methylated cellulose, 47
 from octamethylcellobiose, 44
- Thiobarbituric acid, furfural precipitant, 144
- Thiocitramalic acid lignin, 253, 284
- Thioglycolic acid lignin, 194, 253-254, 284
 molecular weight, 296
- Thiohydraerylic acid lignin, 254
- Thiolactic acid lignin, 253-284
- Thiolignin, 212-213, 482-487
 equivalent weight, 486
 formation, 482
 molecular weight, 484
 oxidative degradation, 488
 water soluble fraction, 487-488
- Thiomalic acid lignin, 253, 284
- Thiophenol lignin, 247
- Thiosulfate
 formation in sulfite process, 424
 use in sulfate process, 488
- Thujaepicin, 344
- Tingle number, 331
- Torula*, cultivation on sulfite waste liquor, 463
- Torus, 5
- Tracheids, 4 ff.
 structures of, 365
- Trimethylcellulose, hydrolysis of, 44
- 2,3,6-Trimethylglucose
 from methylated cellulose, 47
 from octamethylcellobiose, 44
- Tsugalactone (tsugaresinol), 322
- Turpentine
 composition, 334
 sulfate process, yield in, 492
 yields from different woods, 333, 334

U

- Ultracentrifuge methods, 70-74
 molecular weight, determination of, 72
 sedimentation constants, 71-72
 sedimentation equilibrium, 71
 sedimentation velocity, 71

V

γ -Valerolactone, formation in dry distillation of cellulose, 108

Vanillic acid

dry distillation of lignin, formation in, 268

lignin, alkaline oxidation of, formation in, 214, 280, 306, 310

lignosulfonic acid, caustic fusion, formation in, 227, 235

sulfite waste liquor, preparation from, 466-467

Vanillin

coniferaldehyde decomposition product, 190

dry distillation of lignin, formation in, 268

lignin, alkaline oxidation of, formation in, 214, 280, 306, 310

lignosulfonic acid, formation from, 229-235

model substances, formation from, 232

phenol lignin degradation, formation in, 247

sulfite waste liquor, preparation from, 466-467

Vanillin-5-carboxylic acid, 280, 307, 310

Vanilloylmethyl ketone, 242

Vanillyl alcohol, 207

Vanillyl disulfide, 485

Veratraldehyde

methyalted lignosulfonic acid, formation from, 229

Veratric acid

cuproxam lignin, formation from, 277

lignin degradation, formation in, 279, 306, 310, 311

Veratroylformic acid, from cuproxam lignin, 277

Veratryl alcohol, 203, 207

Veratrylethylether, 203

Vessels, 2 ff.

Viscosity

concentration, effect of 70

Einstein equation, 67

linear particles, 68

K_m constant, 68

spherical particles, 67

Staudinger equation, 68

W

Water

conduction of, in hardwoods and softwoods, 18

wood, content of, 32-34, 352, 548-552

Wax in wood, 357

White rot fungi, 558, 559

White wood, 24

Wiesner reaction, 183 ff., 194

Willstätter lignin (see Hydrochloric acid lignin)

Wood (See also names of species, Heartwood, Sapwood, Springwood, Summerwood)

acetaldehyde, from, 234

acetolysis, 299, 301

acetyl bromide, treatment with, 299

acetyl groups, 356-357

acid hydrolysis, 390-413

aging, 548

alcoholysis, 237-247

alkaline pressure heating, 543-547

alkaloids in, 347

analyses, 17, 37, 350-358

anatomy, 1 ff.

annual rings, 1, 14, 28

araban, 142-144

arabogalactan, 152

ash content and composition, 17, 37, 351, 354

bacteria, action of, 109-116

balsams, 333 ff.

behavior during storage, 548-552

brown rot, 561

caustic fusion, 540-543

cellulose content, 350-358

chemical composition, 37, 350-358

chlorine gas, treatment with, 502

chlorine water, treatment with, 502

color reactions, 181-193

Combes reaction, 192

compressive strength, 29

coniferaldehyde groups in, 189-190, 288

cuprammonium solution, effect of, 301

density, 21

diazomethane, action of, 311

drying, 32-36

dyes, occurrence of, 345-346

elementary composition, 37

enzymatic degradation, 109-116

fats, presence of, 332-335, 350-351

fatty acids, presence of, 335

fiber saturation, 34-36

fructan, 153, 356, 357

fructose, determination of, 131

fungi, action of, 558 ff.

furfural from hydrolysis of, 395, 400

galactan, determination of, 151-152

hemicelluloses, 350-358

hot water, influence of, 550

hypobromite, action of, 215

inorganic constituents in, 347-349

lignin, location of, 297-306

Mäule reaction, 193, 215

mannan, determination of, 145-147

methoxyl content, 352-355

methyalted, sulfite cooking of, 212

- Wood (*continued*)
- methylation, 212, 299, 311
 - methyl number, 351
 - moisture content, 32-34, 352, 548-552
 - natural decomposition, 553-564
 - nitration, 299
 - nitric acid, treatment with, 503-504
 - nitrogen content, 17, 347, 351
 - nitrogen dioxide, treatment with, 503
 - oxalic acid from caustic fusion, 540-543
 - pectin, determination of, 155
 - pentosan content, 17, 350-357
 - phenol uptake, 184
 - physical properties, 28-36
 - polyuronic acids in, 356
 - potassium-liquid ammonia, treatment with, 302
 - prehydrolysis followed by sulfate pulping, 489
 - pressure hydrogenation, 274-275
 - proteins in, 17, 351, 356, 357
 - pyridine-sulfur trioxide, treatment with, 302
 - red rot, 558, 559, 561
 - resins in, 350-357
 - saltpeter, treatment with, 503
 - shrinkage, 35
 - skeletal substance, 349
 - specific gravity, 29
 - spontaneous combustion of stored chips, 538
 - stability against acids and bases, 550-551
 - stannous chloride, treatment with, 184
 - steam and hydrogen peroxide, treatment with, 182
 - swelling, 36
 - tannins in, 17, 343, 347
 - tars and phenols, digestion with, 546-547
 - thermal decomposition, 531-539
 - vanillin from, 234
 - water content, 32-34, 352, 548-552
 - water, hydrolytic degradation by, 105-106
 - white rot, 558, 559
 - xanthation, 64
 - xylan, determination of, 137 ff.
- Wood analysis, 17, 37, 350-358
- Wood cells
- different, physiological function of, 17-19
 - relative amounts of 7-11
- Wood distillation
- addition of chemicals, 537
 - charcoal, composition of, 533, 538
 - gas formation, 534-537
 - pyroligneous acid, 535
 - reactions in, 532-537
 - temperature effect of, 537
 - thermochemistry of, 537-538
 - two-stage reaction, 532-533
 - yields of distillation products, 533-537
- Wood fibers
- average length and breadth of, 20-24
 - constitution of, and pulp properties, 24
- Wood gum, 120, 137
- Wood polyoses (see also Pentosan, Arabin, Mannan, Glucan, Galactan, Fructan, Pectin, Polyuronic acids)
- classification, 134-137
 - definition, 39
 - degree of polymerization, 137
 - occurrence in different woods, 157
 - spruce holocellulose, components in, 152
 - sulfite waste liquor, occurrence in, 156
 - wood, content of, 350-358
 - wood, determination in, 156-160
- Wood saccharification
- alcohol, yield of, 392 ff.
 - American process, 398
 - Ant-Wuorinen process, 397
 - butanol, formation of, 399
 - 2,3-butylene glycol, formation of, 399
 - p*-cymene, formation of, 395
 - dilute acid methods, 391-400
 - effect of catalysts, 394
 - fermentable sugar, yield of, 393, 396
 - furfural, formation of, 395
 - gaseous hydrochloric acid, 411
 - hydrochloric acid methods, 402-411
 - hydrogen fluoride methods, 410
 - lignin residue, 400
 - Madison wood sugar process, 399
 - methyl alcohol, formation of, 395
 - α -pinene, formation of, 395
 - reaction velocity, 398
 - reducing sugar, yield of, 393, 396
 - Rheinau process, 391, 404-408
 - Scholler process, 390, 396-397
 - sulfuric acid methods, 400-402
 - terpenes, formation of, 395
 - yeast, production of, 399
- Wood tissue
- chemical composition of different parts, 17
 - growth of, 11-17
- X
- Xylans
- acetyl groups in, 105
 - degree of polymerization, 140
 - determination, 106 ff.
 - methylation of, 142
 - polydispersity, 142
 - viscosity of solutions, 68
 - wood, content of, 356-357

Xylose

isolation from sulfite waste liquor,
138-140
isolation from wood, 138-140
preparation from seed husks, 120
Rheinau process, yield in, 407

Y

Yeast

production from sulfite waste liquor,
463-464
production from wood sugar, 399

Z

Zinc chloride, hydrolysis of cellulose with,
90
Zinc chloride-formic acid, solubility of
cellulose in 85-86
Zinc chloride-iodine, color reaction with
polysaccharides, 25, 41
Zinc dust, distillation of lignin with, 258,
274



checked
19/12/89

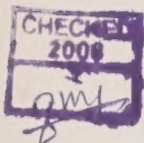
MA
16/4/92

18/3/89

C. F. T. R. I. LIBRARY, MYSORE.

Acc. No. 4190

Call No. E1,58761J NSI

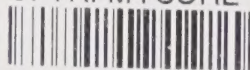


Please return this publication on or before the last DUE DATE stamped below to avoid incurring overdue charges.



Due Date	Return Date	Due Date	Return Date	Due Date	Return Date
23.9.83	12.9.83				
19/10	19/10				
6/11	7.11.83				
22.11.83	22.11.83				
7.12.83	21/12				
22/12	21/12				
25.1.84	25/1				
13 6 96	13/4				

CFTRI-MYSORE



4190
Chemistry of woo

